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(19) **United States**(12) **Patent Application Publication****Kodenkandath et al.**(10) **Pub. No.: US 2007/0197395 A1**(43) **Pub. Date: Aug. 23, 2007**(54) **METHOD OF PATTERNING OXIDE
SUPERCONDUCTING FILMS****Related U.S. Application Data**

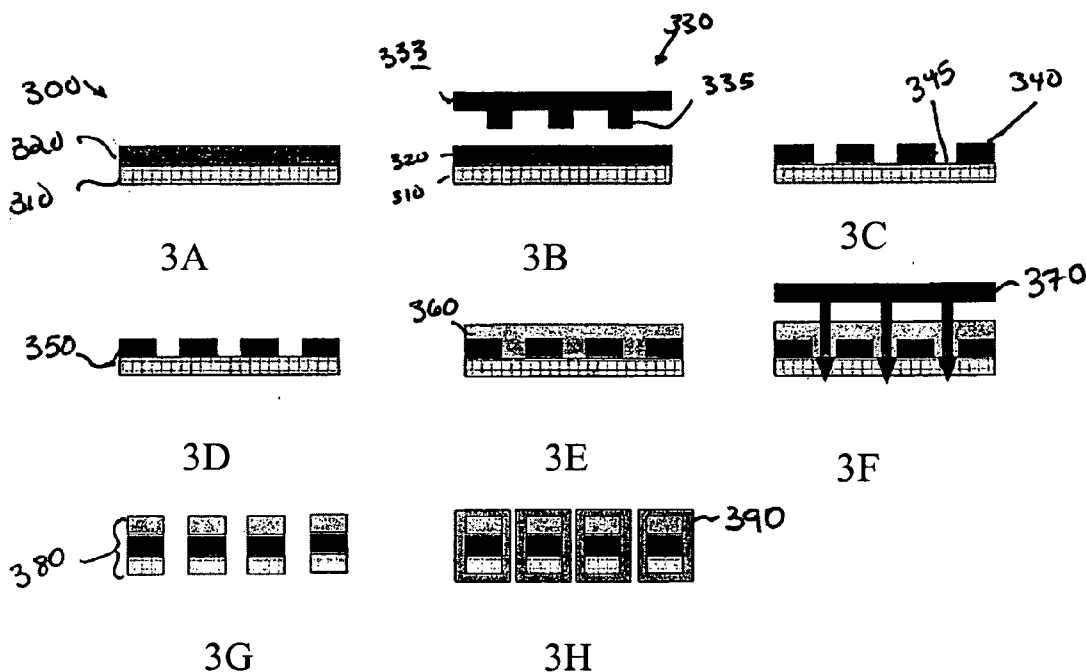
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BOSTON, MA 02109 (US)**(57) **ABSTRACT**

A process for preparing a superconductor article includes depositing a precursor solution onto a substrate to form a precursor film, the precursor solution comprising precursor components to a rare earth-alkaline earth metal-transition metal oxide in one or more solvents, decomposing the precursor film to form an intermediate film comprising the rare earth metal, the alkaline earth metal, and the transition metal of the first precursor solution, selectively removing portions of the intermediate film, wherein a patterned intermediate film is obtained, and treating the patterned intermediate film to form a rare earth-alkaline earth metal-transition metal oxide superconductor.

(73) Assignee: **American Superconductor Corpora-
tion**, Westborough, MA(21) Appl. No.: **11/651,911**(22) Filed: **Jan. 10, 2007**

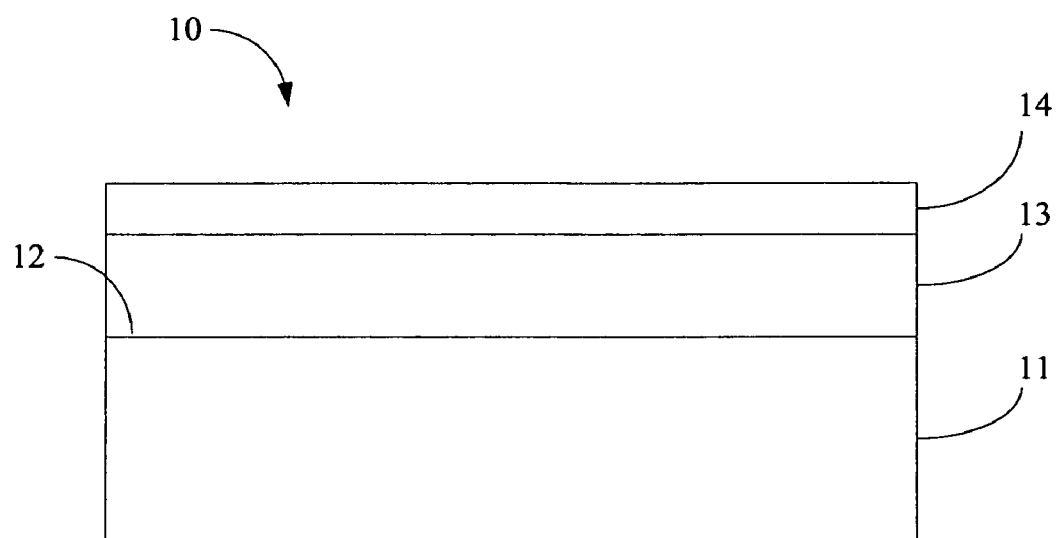


Figure 1

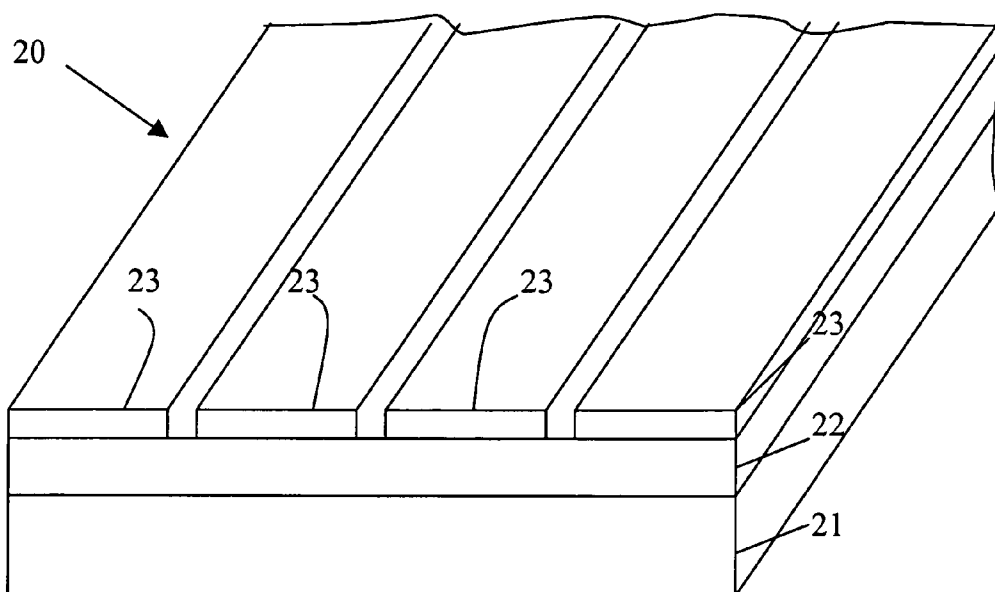


Figure 2A

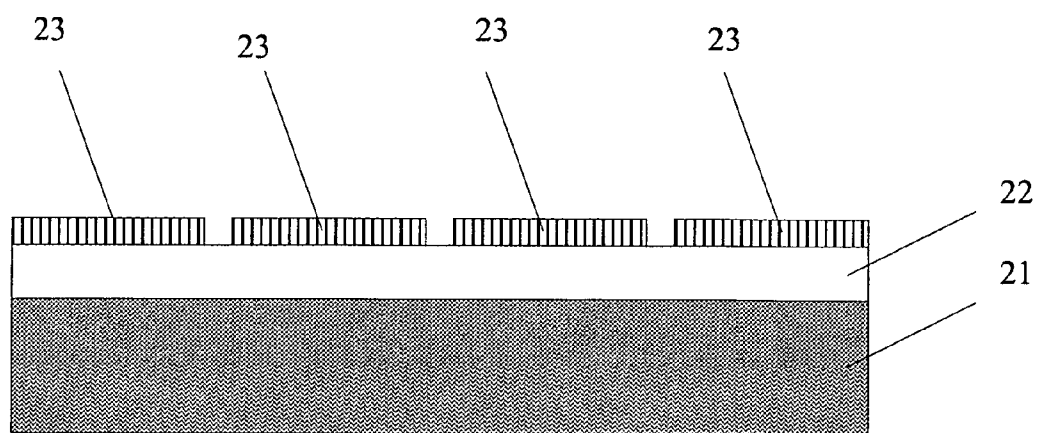


Figure 2B

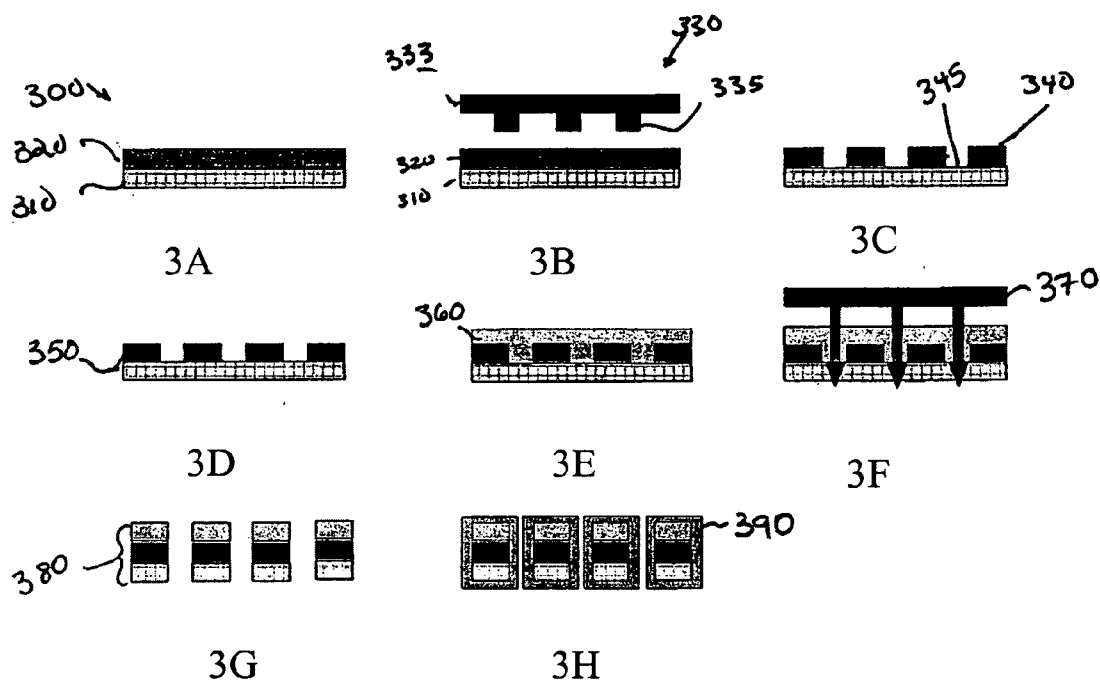


Figure 3

Figure 4A

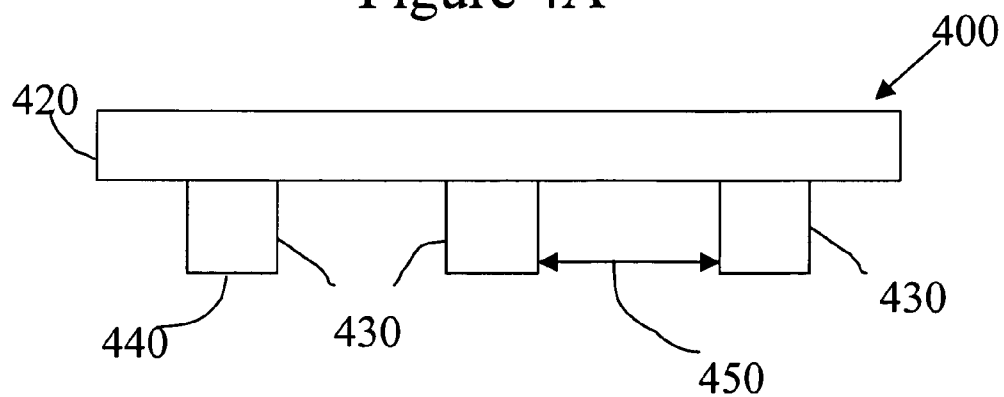


Figure 4B

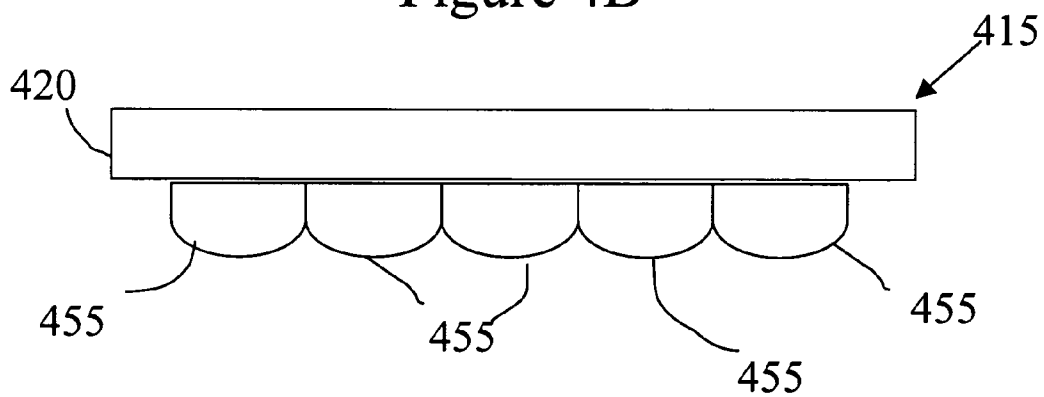


Figure 4C

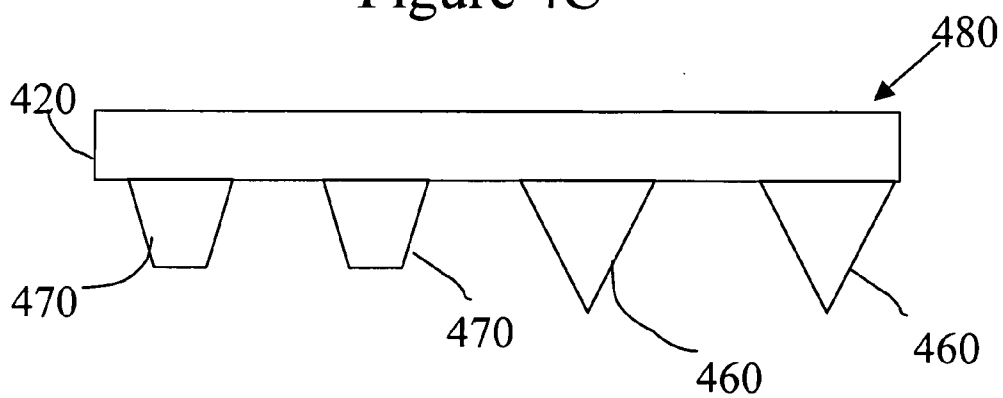
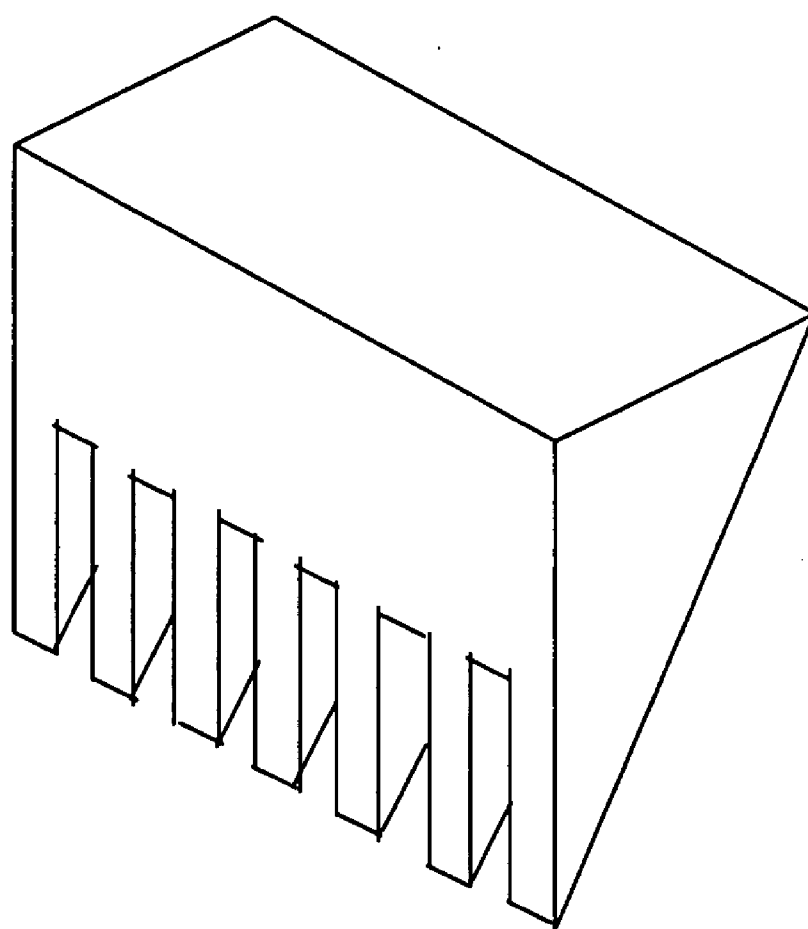


Figure 4D



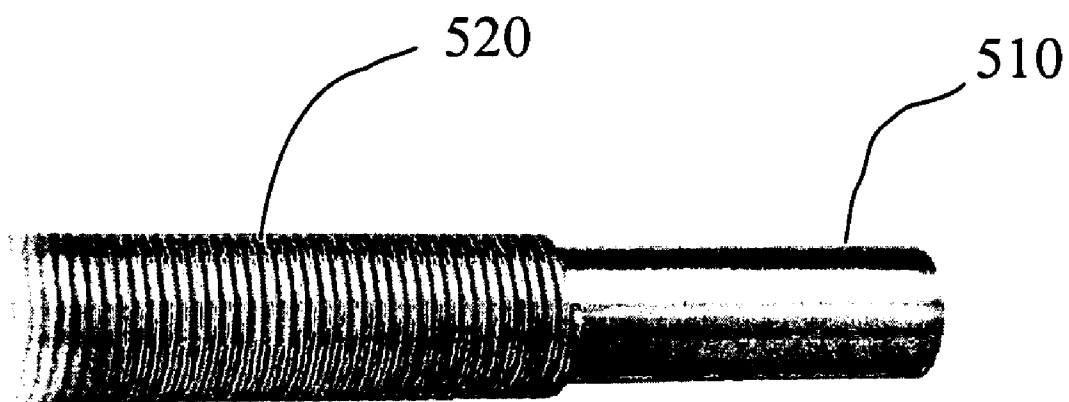


Figure 5A

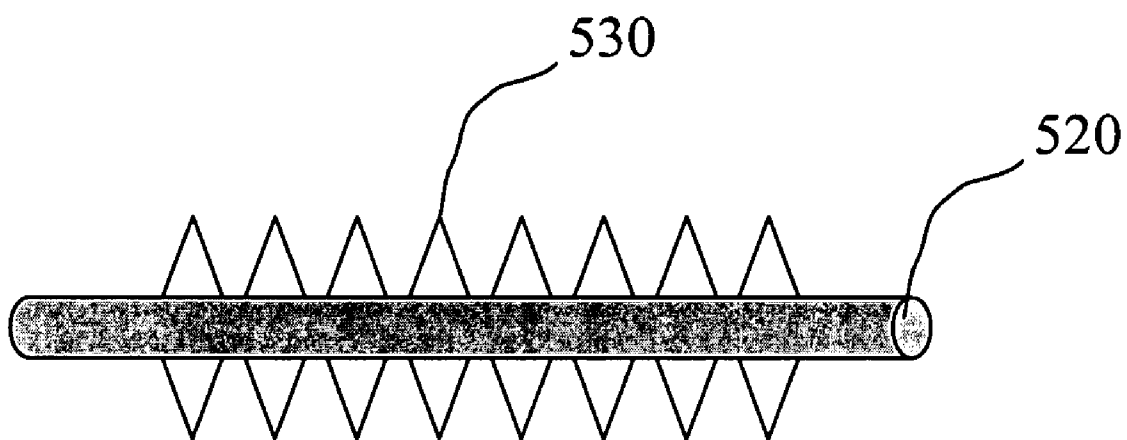
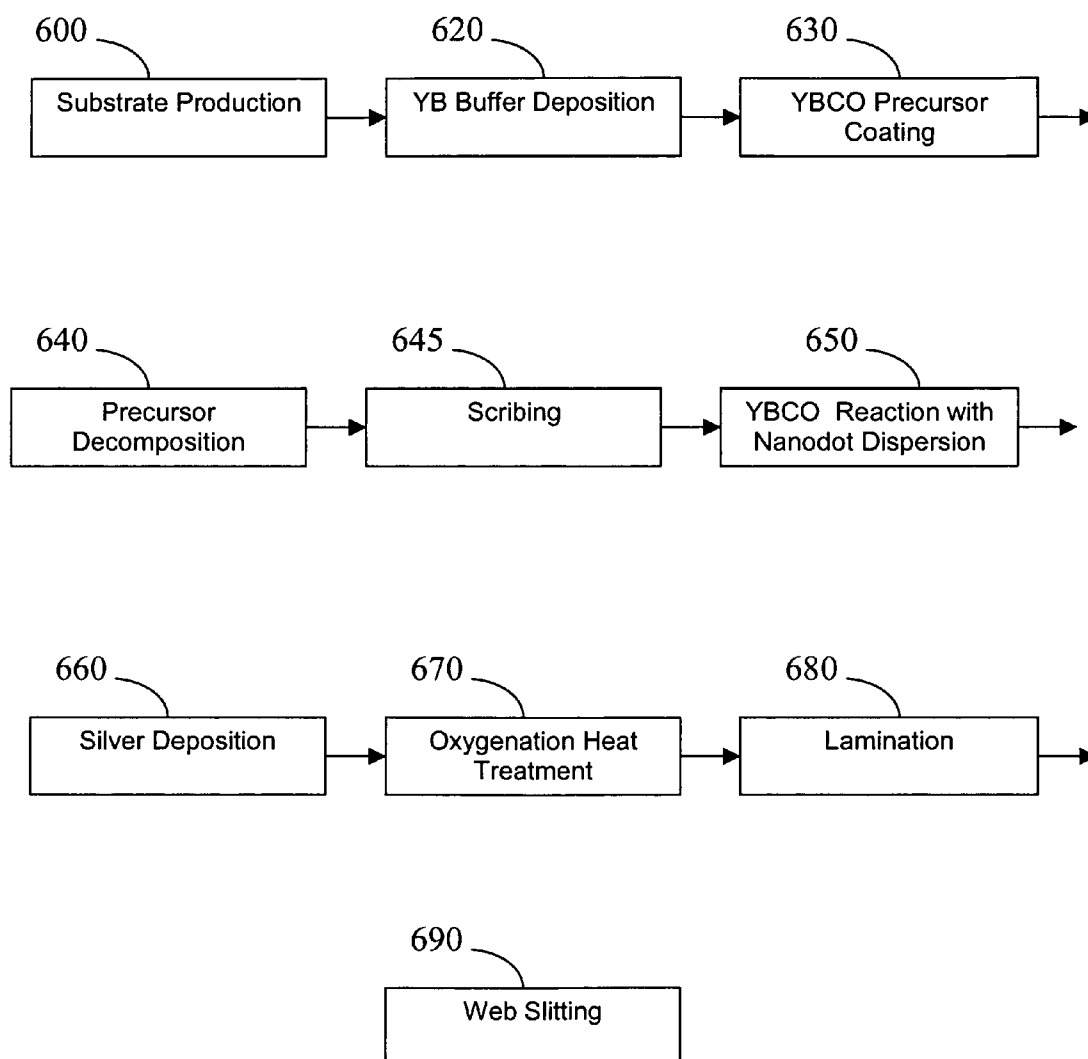


Figure 5B

Figure 6



METHOD OF PATTERNING OXIDE SUPERCONDUCTING FILMS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit under 35 U.S.C. §119(e) of U.S. Provisional Patent Application No. 60/757,855, filed on Jan. 10, 2006, entitled Method of Patterning Oxide Superconducting Films, which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] 1. Field of the Invention

[0003] This invention relates to methods of manufacturing high temperature superconductor ("HTS") wire. In particular, the invention relates to facile methods for patterning long lengths of high temperature superconductor wire. The invention also relates to methods and superconductor articles suitable for use in alternating current (ac) and time varying magnetic field applications. Additionally the invention relates to methods to a securely slit HTS strips processed in wider widths to narrow wires to meet industry requirements.

[0004] 2. Background of the Invention

[0005] Since the discovery of high-temperature superconducting (HTS) materials (superconducting above the liquid nitrogen temperature of 77 K) there have been efforts to develop various engineering applications using such HTS materials. In thin film superconductor devices and wires, significant progress has been made with fabrication of devices utilizing an oxide superconductor including yttrium, barium, copper and oxygen in the well-known basic composition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (hereinafter referred to as "YBCO"). Biaxially textured superconducting metal oxides, such as YBCO, have achieved high critical current densities in a coated conductor architecture, often referred to as second generation HTS wires, or a "coated conductor." The expression "HTS wire" indicates a HTS conductor with attributes that make it useful for the construction of a superconducting device; its cross-sectional geometry can vary from tape-like to round.

[0006] Typically, second generation HTS wires **10** include a metal substrate **11**, buffer layer(s) **13**, and an active layer **14**, e.g., a superconductor, as illustrated in FIG. 1. The metal substrate, such as Ni, Ag, or Ni alloys, provides flexibility for the article and can be fabricated over long lengths and large areas. The metal can include a textured surface **12** for producing an epitaxially grown layer. The buffer layer(s) consists of metal oxide layers, such as LaAlO_3 , Y_2O_3 , CeO_2 , or yttria-stabilized zirconia (YSZ) and serves as a chemical barrier layer between the metal substrate and the active layer. The buffer layer(s) reduces oxidation of the substrate and also reduces the diffusion of chemical species between the substrate and the superconductor layer. Moreover, the buffer layer(s) can have a coefficient of thermal expansion that is well matched with the superconductor material. A RABiTS™ (rolling-assisted, biaxially textured substrates) textured template is typically used. A RABiTS™ substrate is a roll-textured and annealed metal tape, e.g., nickel or nickel alloy such as NiW with a sharp cube texture, covered in an epitaxial manner with one or more oxide or metal buffer or

conditioning layers. Another variation used to prepare the textured template is ion beam assisted deposition or IBAD. The resulting textured base serves as a template for the HTS compound, e.g., yttrium-barium-copper-oxide (YBCO).

[0007] In large-scale production, the second generation HTS wires will be continuously processed as strips that are four or more centimeter wide and 100 s of meters long. Once the process is complete, the wide strip will be cut or slit into narrower wires, typically about 4 mm in width (a current industry standard). Thus, eight or more HTS wires can be obtained from each processed strip, thereby significantly reducing the processing costs.

[0008] Slitting of a coated conductor is challenging due to the many different mechanical properties of the different metal/alloys and ceramic oxides of the coated conductor. In particular, the oxide superconductor is very brittle, and the conventional slitting processes may damage the edge of the superconducting layer causing cracks or delamination of HTS layer. If the oxide superconductor is damaged during slitting, the electrical and mechanical properties of the conductor may be degraded.

[0009] Many potential applications for HTS wire involve operating the superconductor in the presence of ramped magnetic or oscillating magnetic fields, or require that the HTS wire carry alternating current. In the presence of time-varying magnetic fields or currents, there are a variety of mechanisms that give rise to energy dissipation, hereinafter referred to as "ac losses." Although second generation HTS wire is currently suitable for many types of electric power devices, including power transmission cables and rotor sections of motors, the ac losses from the current HTS wires are too high for use in demanding HTS applications in which the alternating magnetic fields have a higher amplitude or frequency. The use of an HTS wire with greatly reduced ac losses would enhance the application of these wires in a variety of novel, HTS-based devices.

[0010] It has been proposed to divide an oxide superconducting film into narrow filaments to suppress ac loss in a superconducting oxide thin film. FIG. 2A is a perspective view of a portion of a coated conductor article in which the superconducting film is arranged as a thin filament array. The multilayer article **20** includes a metal substrate **21** having a textured surface and epitaxially grown buffer layer(s) **22**. Superconductor filaments **23** run substantially continuously along the length of the base to form an array of substantially parallel filaments.

[0011] Currently, many different approaches are being explored to create oxide superconductor filaments, including laser patterning, sand blasting, direct ink-jet printing and photolithography, most of which are carried out after the oxide superconductor has already been formed. Each of the methods are limited in some respect by the cost of the process, damage caused to the oxide superconductor and its feasibility in a continuous process.

SUMMARY

[0012] Methods for patterning superconductor films are described. The methods provide narrow HTS wires from wide coated strips without detriment to the performance of the superconductor wire. The methods also provide HTS wires having narrow filaments for improved ac loss.

[0013] In one aspect of the invention, a method for preparing a superconductor article includes depositing an intermediate metaloxy, e.g., metal oxyfluoride, film on a substrate, the intermediate metaloxy fluoride film containing precursor components to a rare earth-alkaline earth metal-transition metal oxide; removing selected portions of the intermediate metaloxy fluoride film from the substrate to obtain a patterned intermediate film; and treating the patterned intermediate film to form a rare earth-alkaline earth metal-transition metal oxide superconductor.

[0014] In one or more embodiments, the intermediate film is deposited from a precursor solution onto a substrate to form a precursor film, the precursor solution containing precursor components to a rare earth-alkaline earth metal-transition metal oxide in one or more solvents, and decomposing the precursor film to form an intermediate film containing the rare earth metal, the alkaline earth metal, and the transition metal. The precursor solution includes a mixture of at least one rare earth element cation, an alkaline earth metal cation, and of a transition metal cation. The intermediate film can be a metal oxyfluoride film greater than 2 μm in thickness.

[0015] In one or more embodiments, the intermediate film is deposited by e-beam deposition.

[0016] In one or more embodiments, the step of removing selected portions of the intermediate film includes contacting a tool with the intermediate film, the tool having a plurality of scribing surfaces, and removing selected regions of the intermediate film at contact points of the scribing surfaces with the film.

[0017] In one or more embodiments, the scribing surface of the tool comprises a plurality of protrusions, or the plurality of scribing surfaces are positioned on a base to provide scribing surfaces spaced apart at distances commensurate with the width of a high temperature superconductor wire, or the plurality of scribing surfaces are arranged on a base to provide scribing surfaces spaced apart at distances commensurate with the width of a high temperature superconductor filament, or the scribing surfaces have a base and a tip, and the tip-to-tip distance is commensurate with the width of a high temperature superconductor wire, or the scribing surfaces have a base and a tip, and the tip-to-tip distance is commensurate with the width of a high temperature superconductor filament. A wire is an article that contains at least one superconductor filament.

[0018] In one or more embodiments, the scribing surfaces have a base and a tip and the tip is rounded, or the tip is truncated or flattened to increase area contact of the tip with the intermediate film.

[0019] The step of removing selected portions from the intermediate film can include a materials removal step selected from the group consisting of mechanical removal, chemical etching, laser etching and physical bombardment.

[0020] In some embodiments, the patterned film includes a plurality of longitudinally located regions of HTS or intermediate material having gaps between regions and the gaps have a width of about 0.1 to about 0.5 mm.

[0021] In some embodiments, the patterned intermediate film is a filament array having a plurality of HTS or intermediate material filaments extending substantially

along the length of the substrate and spaced apart from adjacent filaments across the width of the substrate. The article includes about 2 to about 100 filaments and the filaments are about 50 to 5000 μm in width, and the gap is between 10 and 100 μm .

[0022] In one or more embodiments, the method further includes rinsing the surface of the scribed intermediate metaloxy fluoride film to remove scribed material. The method may also further include coating the patterned oxide superconductor with a protective layer and slitting the patterned oxide superconductor strip. The patterned oxide superconductor strip is slit into wires having a width in the range of about 1 mm to 8 mm, and the slitting occurs at a region of the film where the intermediate film has been removed.

[0023] In some embodiments, the precursor film is decomposed to form an intermediate film by heating the film at a temperature in the range of about 190° C. to about 650° C., or by heating the film at a temperature in the range of about 190° C. to about 400° C.

[0024] In some embodiments, the patterned intermediate metaloxy fluoride film is converted into an oxide superconductor by heating at a temperature in the range of about 700° C. to about 825° C. in an environment having a total pressure of about 0.1 Torr to about 760 Torr and containing about 0.09 Torr to about 50 Torr oxygen and about 0.01 Torr to about 150 Torr water vapor.

[0025] In some embodiments, the substrate is biaxially textured; and the superconductor film is biaxially textured and has a c-axis orientation that is substantially constant across its width, the c-axis orientation of the superconductor film being substantially perpendicular to the surface of the substrate. The article also includes at least one buffer layer containing a material selected from the group consisting of cerium oxide, lanthanum aluminum oxide, lanthanum manganese oxide, strontium titanium oxide, magnesium oxide, neodymium gadolinium oxide, yttrium oxide and a gadolinium zirconate, lanthanum zirconate, yttria-stabilized zirconia, rare earth oxides or rare earth zirconates disposed between the substrate and the oxide superconductor layer.

[0026] In another aspect of the invention, an oxide superconducting tape is provided having a biaxially textured substrate greater than 1 cm, or greater than 4 cm, in width; and a patterned superconducting layer deposited on the substrate, wherein the superconducting layer includes a rare earth barium copper oxide superconductor, the pattern defining a plurality of parallel stripes of oxide superconductor each having a width of at least 1 mm. The overall thickness of the intermediate film is typically about 2 μm or greater and the overall thickness of the superconductor film is typically greater than about 0.8 μm .

[0027] In some embodiments, the oxide superconducting stripes have width of about 1-8 mm separated by gaps with a width of about 0.1 to about 0.5 mm. The strip includes a biaxially oriented substrate and a biaxially textured buffer layer stack consisting of yttrium oxide, yttria-stabilized zirconium oxide and cerium oxide.

[0028] In another aspect of the invention, a metal oxyfluoride tape includes a biaxially textured substrate greater than 1 cm, or greater than 4 cm, in width; and a patterned metal oxyfluoride layer deposited on the substrate, wherein

the metal oxyfluoride layer includes at least a rare earth metal, an alkaline earth metal, and a transition metal of a rare earth barium copper oxide superconductor, the pattern defining a plurality of parallel stripes of metal oxyfluoride each having a width of at least 1 mm. The metal oxyfluoride stripes have width of about 1-8 mm.

[0029] In one or more embodiments, a patterned oxide superconductor tape is converted into narrower wires by cutting the tape through regions where the oxide superconductor has been removed. The method also includes depositing protective layer over at least the patterned oxide superconductor; and slitting the patterned oxide superconductor strip through the gaps defined by the pattern, wherein the slit tape forms wires having a protective layer covering the patterned superconductor. The protective layer may form a continuous layer over the patterned oxide superconductor strips or a discontinuous layer over the strips alone.

[0030] In certain embodiments, a continuous layer is applied for protection during splitting the patterned oxide superconductor tape into narrower strips. In certain embodiments, e.g., for filamentized superconducting oxide strips for use as ac conductors, a protective layer, e.g., silver is deposited only onto the surface of the superconductor filaments.

BRIEF DESCRIPTION OF THE DRAWING

[0031] The invention is described with reference to the following figures, which are presented for the purpose of illustration only and which are not intended to be limiting of the invention and in which like elements are indicated by the like numbers in all the figures.

[0032] FIG. 1 is a cross-sectional view of a typical superconductor article.

[0033] FIG. 2A is a perspective view of a coated conductor article, in which the HTS film is arranged as a thin filament array; and FIG. 2B is a cross-sectional view of a coated conductor article, in which the HTS film is arranged as a thin filament array, with a common stabilizer layer.

[0034] FIGS. 3A-3H provide a schematic illustration of a patterning process and slitting according to one or more embodiments of the present invention.

[0035] FIGS. 4A-4D are a cross sectional and perspective illustrations of scribing instruments for use in one or more embodiments of the present invention.

[0036] FIG. 5A-5B are illustrations of Mayer rods used to demonstrate scribing of a decomposed precursor film according to one or more embodiments of the invention.

[0037] FIG. 6 is a schematic illustration of a system and process used to prepare a textured, patterned oxide superconductor wire according to one or more embodiments of the invention.

DETAILED DESCRIPTION

[0038] A metal organic (solution based) deposition (MOD) process represents an attractive system to obtain superconducting films because the precursor solution is versatile and can be varied over a wide range of compositions and concentrations. In an MOD process, precursor solutions containing suitable metal-containing precursors

are decomposed to form an intermediate composition containing the constituent metals of the final oxide superconductor. In some instances the intermediate composition includes metal oxides. In other instances where the precursor solution contains halides, and in particular fluoride, the intermediate composition includes a metal oxyhalide, e.g., a metal oxyfluoride. In a typical process, an MOD solution is deposited onto a substrate and decomposed to form an intermediate metaloxy (or metal oxyfluoride) film prior to formation of the oxide superconductor film. The decomposed metal oxy film is soft and ductile.

[0039] The intermediate metaloxy or metaloxy fluoride films may also be obtained using e-beam or pulsed e-beam deposition of oxygen and the constituent metal elements to an oxide superconductor. Electron beam deposition uses the heat generated by electron beams striking the solid surfaces to evaporate yttrium, barium, and copper for physical vapor deposition (PVD) of YBCO thin films which have high-temperature superconducting properties. The three metals are evaporated by the electron beam guns while atomic oxygen is pumped in for oxidation of the elements. When a metal fluoride source is used as a target, a metal oxyfluoride intermediate film is deposited.

[0040] The methods described herein take advantage of the less brittle nature of the decomposed precursor (as compared to the final oxide superconductor), and the intermediate metaloxy or metal oxyfluoride film is patterned by removing selected portions of the film at this stage of the process. Due to the less brittle nature of the film, the patterning process does not cause as much damage to the intermediate film as is observed for the oxide superconductor. Furthermore, any damage that does occur can be corrected during later processing of the intermediate film into an oxide superconductor.

[0041] The patterning process is selected to remove material from predetermined portions of the film. Exemplary materials removal processes include etching processes, such as mechanical removal, chemical etching, physical bombardment and plasma ion bombardment. The soft, malleable intermediate film is more readily removed using these techniques than is the brittle oxide superconductor. The patterning process also includes mechanically removing material from the intermediate film surface using an instrument capable of cutting, notching, or scoring the film.

[0042] A mechanical patterning process is described with reference to FIG. 3. The process illustrates the mechanical scribing and subsequent processing of a metal strip and its slitting into narrower HTS wires. In one or more embodiments, the strip 300 is at least about 4 cm wide, although wider strips, e.g., 10 cm or higher, may be used.

[0043] FIG. 3A shows a simplified cross-section of a coated article 300 having substrate 310 (which typically contains one or more buffer layers) (not shown) and an intermediate metaloxy or metaloxy fluoride layer 320. The metaloxy film layer 320 is obtained by appropriate heat treatment to decompose a previously deposited MOD precursor layer (described in greater detail below) or by e-beam deposition of a metaloxy or metal oxyfluoride film. The metaloxy film is considerably more malleable than the resultant oxide superconductor.

[0044] After the intermediate layer has been formed and before the intermediate layer is processed into an oxide

superconductor, e.g., while still malleable, the film is patterned by any suitable means, for example, by mechanically removing material from the intermediate film surface using a scribing tool, as is illustrated in FIG. 3B. The scribing tool 330 includes a base 333 and a number of protrusions or scribing elements 335. The protrusions 335 are pressed into the film surface to remove the intermediate metal-oxide film at contact points with the tool as the scribing tool is moved with respect to the film surface (or the film surface moves beneath the scribing tool). The scribing tool can be connected to a computer-controlled X-Y stage and programmed to create a pattern of any choice (and of any length) including straight lines or other patterns, e.g., curves or diagonal patterns. The scribing step forms a patterned film 340 by removing material and leaving a gap 345 where there is no intermediate layer material. Thus, the intermediate layer is inscribed, etched, carved or otherwise patterned by the tool to provide a patterned film 340, as illustrated in FIG. 3C. The carved-out material can be removed from the film surface before further processing, for example, by airflow over the film surface, rinsing in an inert solvent such as methanol or other conventional techniques.

[0045] Mechanical scribing of the intermediate layer can remove the entire intermediate layer under the scribe so as to expose the underlying buffer layers. It is appreciated that the scribe does not score the intermediate layers in a way that would damage the underlying layers or otherwise impair the mechanical integrity or strength of the substrate or such that the article is otherwise negatively affected. In other embodiments, a thin layer of the intermediate layer may remain after scribing; however, it is sufficiently thin that it does not impair subsequent slitting of the fully reacted HTS film.

[0046] In one or more embodiments, the intermediate patterned film forms longitudinally arranged stripes having gaps between stripes. The stripes can be greater than about 1 mm wide, for example, about 1 mm to 8 mm, and the gaps between the stripes can have a width of about 0.1 to about 0.5 mm. Because the patterning of the superconductor layer is large (e.g., on the order of millimeters), this process is referred to as "macro-scribing."

[0047] In some embodiments, fine filament patterns are produced in the intermediate film and the amount of scribed material is very small. These filamentized films are useful in creating HTS filaments for ac applications. The patterned intermediate film forms a filament array having a plurality of filaments extending substantially along the length of the substrate and spaced apart from adjacent filaments across the width of the substrate. The filaments are about 50 to 5000 μm in width, and the gap between adjacent filaments is between 10 and 100 μm . Because the patterning of the superconductor layer is on a fine scale (e.g., on the order of microns), this process is referred to as "micro-scribing."

[0048] The patterned intermediate oxide film then is converted into a patterned oxide superconductor film 350 as illustrated in FIG. 3D by appropriate heat treatment (described in greater detail below). The patterned oxide superconductor film is coated with a protective layer 360 in a deposition step as illustrated in FIG. 3E. The HTS film 350 now contains gaps 345 filled in at least partially by the inert protecting layer 360. Because the protective layer is in direct contact with the HTS layer in the current embodiment, the

protective layer is desirably inert to the HTS material. Typically, the protective layer includes a noble metal such as silver. Silver can be deposited by a variety of methods including evaporation, sputtering, solution deposition and other methods. The protective layer may form a continuous layer over the patterned oxide superconductor strips and the exposed buffer layer or a discontinuous layer over the strips or filaments alone.

[0049] In certain embodiments, a protective layer is applied prior to slitting the patterned oxide superconductor tape into narrower strips. In one or more embodiments, the patterned strip may be slit into HTS wires of any desired width; the actual width will depend on the anticipated application for the HTS wire. The coated conductor may be safely slit or cut in the gaps between HTS regions without damage to the HTS material, as illustrated in FIG. 3F. The slitting tool 370 can be a rotating knife or blade with a sharp edge that is smaller in dimension or width than gap 345 so that the slitting takes place through the scribed area (gap) without disturbing the patterned superconductor. Typically, the slitting tool 370 is a cutting wheel having a very narrow width, e.g., less than 2 mm. The slitting tool is equipped with precision guiding to provide the degree of precision needed to slit the strip within the gap. The slitting process provides, for example, silver-coated wires 380 of narrow dimensions; e.g., greater than 1 mm, or about 1-8 mm, or about 4 mm, as is required for a particular application, as illustrated in FIG. 3G. Wires 380 may also contain some degree of silver coating the sides of the superconductor patterned wires (not shown) depending on the relative thickness of the gap and slitting tool.

[0050] The resulting tapes are laminated with a stabilizing layer 390 as illustrated in FIG. 3H. The stabilizing layer 390 is a conductive layer that imparts mechanical robustness to the article. Typically, the stabilizing layer includes copper or stainless steel. In one or more embodiments, the stabilizing layer includes upper and lower conductive stabilizer strips and electrically conductive non-porous filler material, e.g. solder or another low-melting temperature alloy or amalgam, a conductive polymer, or a pure metal such as In. Filler substantially surrounds the HTS tapes and may form a bridge between the stabilizer strips in thick layers on the sides of the wire to thereby complete the isolation of the HTS tape from the surrounding environment and to substantially completely surround the HTS assembly in a conductive structure. Further detail of the laminating step is found in U.S. Pat. No. 6,444,917 and in co-pending and co-owned United States published application 2006/0073979, which are incorporated herein by reference.

[0051] The same approach may be used to pattern an HTS wire to obtain superconducting filaments having reduced ac losses. Typically, a low ac loss HTS wire or tape includes a plurality of oxide superconductor filaments extending substantially along the length of an elongated substrate and spaced apart from other filaments across the width of the elongated substrate. HTS wires may include about 2 to about 100 filaments, and for example, the filaments may have a width of about 50 to 1000 μm . The space between adjacent filaments is in the range of about 10 μm to about 100 μm . Thus, the low ac loss HTS tape is arranged as a thin filament array. See, FIGS. 2A-2B. Alternative embodiments include filaments that periodically cross over one or more filaments. The patterning method is suitable for preparing those por-

tions of the HTS filaments that are coplanar with the substrate, i.e., not the portion of the filament that crosses over another filament. In other embodiments, the HTS filaments vary in their location across the width of the substrate, and may have curvature and/or periodic curvature. Further detail of specific HTS filament patterns are found in United States published application 2006/0040830, entitled "Low Ac Loss Filamentary Coated Superconductor," and United States published application 2006/0073975, entitled "Stacked Filamentary Coated Superconductor," the contents of which are incorporated by reference.

[0052] In one or more embodiments, the filament array is formed by removing material from the soft intermediate film in predetermined regions to form a filament array. Due to the finer scale of patterning of the individual oxide superconductor filaments on an oxide superconductor wire, this process is referred to as "micro-scribing." In those embodiments where material is mechanically removed, the scribing tool includes a base containing a plurality of fine pins or protrusions that are of a dimension to provide the gap spacing and filament widths described above. The scribing tool can be mounted to a computer-controlled X-Y stage and programmed to create a pattern of any choice (and at any length) including straight lines or other patterns that are suitable for reducing ac losses in a superconducting wire.

[0053] In certain other embodiments, e.g., for filamentized superconducting oxide strips for use as ac conductors, a protective layer, e.g., silver, is deposited only onto the surface of the superconductor filaments so as to avoid electrical connectivity between the individual filaments. Exemplary methods for depositing the silver include ink-jet application onto the filaments to cover only the superconductor surface without forming an electrical connection between the HTS filaments, followed by coating an insulating layer in the scribed area to separate the YBCO filaments. Further detail on ink jet printing of silver lines is found at <http://www.microfab.com/technology/energy/energy.html> and T. Kodenkandath, and F. List, "LOW COST FABRICATION OF 2G WIRES FOR AC APPLICATIONS", Final Report Contract No. W31P4Q-05-C-R033, Defense Advanced Research Projects Agency (DOD), Sep. 19, 2005, which are hereby incorporated in their entirety by reference.

[0054] In one or more embodiments, both macro-scribing and micro-scribing are performed. Thus, the intermediate layer of the strip may be first micro-scribed to introduce a filament array across the entire intermediate layer. The micro-scribed layer is then macro-scribed to introduce separations between wire regions on the strip. Location of the macro- and micro-scribed regions can be controlled, e.g., computer-controlled. In other embodiments, the intermediate layer of the coated strip is first macro-scribed to define HTS wire regions, and then micro-scribed to introduce microfilaments on each HTS wire region. Each process can also be used independently.

[0055] An exemplary scribing tool 400 is illustrated in FIG. 4A. The scribing tool 400 has a base 420 and at least one scribing element, surface or protrusion 425 that projects from the base. The protrusion 425 is pressed into the soft intermediate film, and the size and shape of the scribed-out region (gap) is defined, in part, by the size and shape of the tip 440 and sidewalls 430 of the protrusion. The distance 450 between adjacent protrusion tips defines the scribe width of

the scribing tool and defines the width of the HTS wire or tape in macro-scribing or the width of the filament in micro-scribing. The height is referenced against the height of the intermediate film. The height of the actual HTS filament will be significantly less. FIG. 4B shows a cross-sectional illustration of a second example of a scribing tool 415, in which the protrusions 455 are rounded or curved. A further example 480 is shown in FIG. 4C, in which the protrusions may have pointed 460 or flattened 470 tips. FIG. 4D is a perspective illustration of a scribing tool for use in one or more embodiments of the invention. Narrower tips may be suitable for removing small amounts of material during micro-scribing.

[0056] In one or more embodiments, a scribing tool 500 may be a rod 510 that is tightly wound with metallic wire 520. See, FIG. 5A. The wire diameter determines the scribe width. Wire-wound rods are commercially available and typically are used as a coating metering rod (known as "Mayer rods"). Exemplary Mayer rods with about 60 μm and 300 μm wires may be used to scribe the decomposed precursor film. A Mayer rod can also be used for micro-scribing, in which the rod 520 is equipped with sharp edges or multiple fine scribing heads (knives, diamonds, pins etc) 530. See, FIG. 5B. The Mayer Rod has an inherent pitch to the windings. To scribe a continuous length of tape, the rod would have to be angled to compensate for the pitch.

[0057] A web coating method of depositing the precursor film on a textured template having the architecture $\text{CeO}_2/\text{YSZ}/\text{Y}_2\text{O}_3/\text{NiW}$ and processing the precursor film into a patterned oxide superconductor wire is shown in FIG. 6.

Textured Metal Substrate

[0058] The textured template is provided in widths of about 1 to 10 cm. A method of preparing a textured metal substrate suitable for use as a substrate for an HTS coated conductor first is described. At a first station 610, a wire substrate is treated to obtain biaxial texture. Preferably, the substrate surface has a relatively well defined crystallographic orientation. For example, the surface can be a biaxially textured surface (e.g., a (113)[211] surface) or a cube textured surface (e.g., a (100)[011] surface or a (100)[001] surface). Preferably, the peaks in an X-ray diffraction pole figure of surface 110 have a FWHM of less than about 20° (e.g., less than about 15°, less than about 10°, or from about 5° to about 10°).

[0059] The surface can be prepared, for example, by rolling and annealing. Surfaces can also be prepared using vacuum processes, such as ion beam assisted deposition, inclined substrate deposition and other vacuum techniques known in the art to form a biaxially textured surface on, for example, a randomly oriented polycrystalline surface. In certain embodiments (e.g., when ion beam assisted deposition is used), the surface of the substrate need not be textured (e.g., the surface can be randomly oriented polycrystalline, or the surface can be amorphous).

[0060] The substrate can be formed of any material capable of supporting a buffer layer stack and/or a layer of superconductor material. Examples of substrate materials that can be used as the substrate include for example, metals and/or alloys, such as nickel, silver, copper, zinc, aluminum, iron, chromium, vanadium, palladium, molybdenum and/or their alloys. In some embodiments, the substrate can be

formed of a superalloy. In certain embodiments, the substrate can be in the form of an object having a relatively large surface area (e.g., a tape or a wafer). In these embodiments, the substrate is preferably formed of a relatively flexible material.

[0061] In some of these embodiments, the substrate is a binary alloy that contains two of the following metals: copper, nickel, chromium, vanadium, aluminum, silver, iron, palladium, molybdenum, tungsten, gold and zinc. For example, a binary alloy can be formed of nickel and chromium (e.g., nickel and at most 20 atomic percent chromium, nickel and from about five to about 18 atomic percent chromium, or nickel and from about 10 to about 15 atomic percent chromium). As another example, a binary alloy can be formed of nickel and copper (e.g., copper and from about five to about 45 atomic percent nickel, copper and from about 10 to about 40 atomic percent nickel, or copper and from about 25 to about 35 atomic percent nickel). As a further example, a binary alloy can contain nickel and tungsten (e.g., from about one atomic percent tungsten to about 20 atomic percent tungsten, from about two atomic percent tungsten to about 10 atomic percent tungsten, from about three atomic percent tungsten to about seven atomic percent tungsten, about five atomic percent tungsten). A binary alloy can further include relatively small amounts of impurities (e.g., less than about 0.1 atomic percent of impurities, less than about 0.01 atomic percent of impurities, or less than about 0.005 atomic percent of impurities).

[0062] In certain of these embodiments, the substrate contains more than two metals (e.g., a ternary alloy or a quaternary alloy). In some of these embodiments, the alloy can contain one or more oxide formers (e.g., Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Th, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb and/or La, with Al being the preferred oxide former), as well as two of the following metals: copper, nickel, chromium, vanadium, aluminum, silver, iron, palladium, molybdenum, gold and zinc. In certain of these embodiments, the alloy can contain two of the following metals: copper, nickel, chromium, vanadium, aluminum, silver, iron, palladium, molybdenum, gold and zinc, and can be substantially devoid of any of the aforementioned oxide formers.

[0063] In embodiments in which the alloys contain an oxide former, the alloys can contain at least about 0.5 atomic percent oxide former (e.g., at least about one atomic percent oxide former, or at least about two atomic percent oxide former) and at most about 25 atomic percent oxide former (e.g., at most about 10 atomic percent oxide former, or at most about four atomic percent oxide former). For example, the alloy can include an oxide former (e.g., at least about 0.5 aluminum), from about 25 atomic percent to about 55 atomic percent nickel (e.g., from about 35 atomic percent to about 55 atomic percent nickel, or from about 40 atomic percent to about 55 atomic percent nickel) with the balance being copper. As another example, the alloy can include an oxide former (e.g., at least about 0.5 atomic aluminum), from about five atomic percent to about 20 atomic percent chromium (e.g., from about 10 atomic percent to about 18 atomic percent chromium, or from about 10 atomic percent to about 15 atomic percent chromium) with the balance being nickel. The alloys can include relatively small amounts of additional metals (e.g., less than about 0.1 atomic percent of

additional metals, less than about 0.01 atomic percent of additional metals, or less than about 0.005 atomic percent of additional metals).

[0064] A substrate formed of an alloy can be produced by, for example, combining the constituents in powder form, melting and cooling or, for example, by diffusing the powder constituents together in solid state. The alloy can then be formed by deformation texturing (e.g., annealing and rolling, swaging, extrusion and/or drawing) to form a textured surface (e.g., biaxially textured or cube textured). Alternatively, the alloy constituents can be stacked in a jelly roll configuration, and then deformation textured. In some embodiments, a material with a relatively low coefficient of thermal expansion (e.g., Nb, Mo, Ta, V, Cr, Zr, Pd, Sb, NbTi, an intermetallic such as NiAl or Ni₃Al, or mixtures thereof) can be formed into a rod and embedded into the alloy prior to deformation texturing.

[0065] In some embodiments, stable oxide formation at the surface can be mitigated until a first epitaxial (for example, buffer) layer is formed on the biaxially textured alloy surface, using an intermediate layer disposed on the surface of the substrate. Intermediate layers include those epitaxial metal or alloy layers that do not form surface oxides when exposed to conditions as established by PO₂ and temperature required for the initial growth of epitaxial buffer layer films. In addition, the buffer layer acts as a barrier to prevent substrate element(s) from migrating to the surface of the intermediate layer and forming oxides during the initial growth of the epitaxial layer. Absent such an intermediate layer, one or more elements in the substrate would be expected to form thermodynamically stable oxide(s) at the substrate surface which could significantly impede the deposition of epitaxial layers due to, for example, lack of texture in this oxide layer.

[0066] In some of these embodiments, the intermediate layer is transient in nature. "Transient," as used herein, refers to an intermediate layer that is wholly or partly incorporated into or with the biaxially textured substrate following the initial nucleation and growth of the epitaxial film. Even under these circumstances, the intermediate layer and biaxially textured substrate remain distinct until the epitaxial nature of the deposited film has been established. The use of transient intermediate layers may be preferred when the intermediate layer possesses some undesirable property, for example, the intermediate layer is magnetic, such as nickel.

[0067] Exemplary intermediate metal layers include nickel, gold, silver, palladium, and alloys thereof. Additional metals or alloys may include alloys of nickel and/or copper. Epitaxial films or layers deposited on an intermediate layer can include metal oxides, chalcogenides, halides, and nitrides. In some embodiments, the intermediate metal layer does not oxidize under epitaxial film deposition conditions.

[0068] Care should be taken that the deposited intermediate layer is not completely incorporated into or does not completely diffuse into the substrate before nucleation and growth of the initial buffer layer structure causes the epitaxial layer to be established. This means that after selecting the metal (or alloy) for proper attributes such as diffusion constant in the substrate alloy, thermodynamic stability against oxidation under practical epitaxial buffer layer growth conditions and lattice matching with the epitaxial

layer, the thickness of the deposited metal layer has to be adapted to the epitaxial layer deposition conditions, in particular to temperature.

[0069] Deposition of the intermediate metal layer can be done in a vacuum process such as evaporation or sputtering, or by electro-chemical means such as electroplating (with or without electrodes). These deposited intermediate metal layers may or may not be epitaxial after deposition (depending on substrate temperature during deposition), but epitaxial orientation can subsequently be obtained during a post-deposition heat treatment.

[0070] In certain embodiments, sulfur can be formed on the surface of the substrate in a surface treatment. The sulfur can be formed on the surface of the substrate, for example, by exposing the intermediate layer to a gas environment containing a source of sulfur (e.g., H_2S) and hydrogen (e.g., hydrogen, or a mix of hydrogen and an inert gas, such as a 5% hydrogen/argon gas mixture) for a period of time (e.g., from about 10 seconds to about one hour, from about one minute to about 30 minutes, from about five minutes to about 15 minutes). This can be performed at elevated temperature (e.g., at a temperature of from about 450° C. to about 1100° C., from about 600° C. to about 900° C., 850° C.). The pressure of the hydrogen (or hydrogen/inert gas mixture) can be relatively low (e.g., less than about one torr, less than about 1×10^{-3} torr, less than about 1×10^{-6} torr) or relatively high (e.g., greater than about 1 torr, greater than about 100 torr, greater than about 760 torr).

[0071] Without wishing to be bound by theory, it is believed that exposing the textured substrate surface to a source of sulfur under these conditions can result in the formation of a superstructure (e.g., a $c(2 \times 2)$ superstructure) of sulfur on the textured substrate surface. It is further believed that the superstructure can be effective in stabilizing (e.g., chemically and/or physically stabilizing) the surface of the intermediate layer.

[0072] While one approach to forming a sulfur superstructure has been described, other methods of forming such superstructures can also be used. For example, a sulfur superstructure (e.g., $c(2 \times 2)$) can be formed by applying an appropriate organic solution to the surface of the intermediate layer by heating to an appropriate temperature in an appropriate gas environment. It can also be obtained by allowing sulfur, which can be added to the substrate material, to diffuse to the surface of the substrate.

[0073] Moreover, while formation of a sulfur superstructure on the surface of the intermediate layer has been described, it is believed that other superstructures may also be effective in stabilizing (e.g., chemically and/or physically stabilizing) the surface. For example, it is believed that an oxygen superstructure, a nitrogen superstructure, a carbon superstructure, a potassium superstructure, a cesium superstructure, a lithium superstructure or a selenium superstructure disposed on the surface may be effective in enhancing the stability of the surface.

Buffer Layer

[0074] In a second processing station 620, a buffer layer is formed on the textured substrate.

[0075] Examples of buffer materials include metals and metal oxides, such as silver, nickel, ThO , CeO_2 , yttria-

stabilized zirconia (YSZ), Y_2O_3 , Gd_2O_3 , $LaAlO_3$, $SrTiO_3$, $LaNiO_3$, $LaCuO_{sub.3}$, $SrRuO_3$, $NdGaO_3$, $NdAlO_3$ and/or nitrides as known to those skilled in the art.

[0076] In certain embodiments, an epitaxial buffer layer can be formed using a low vacuum vapor deposition process (e.g., a process performed at a pressure of at least about 1×10^3 Torr). The process can include forming the epitaxial layer using a relatively high velocity and/or focused gas beam of buffer layer material.

[0077] The buffer layer material in the gas beam can have a velocity of greater than about one meter per second (e.g., greater than about 10 meters per second or greater than about 100 meters per second). At least about 50% of the buffer layer material in the beam can be incident on the target surface (e.g., at least about 75% of the buffer layer material in the beam can be incident on the target surface, or at least about 90% of the buffer layer material in the beam can be incident on the target surface).

[0078] The method can include placing a target surface (e.g., a substrate surface or a buffer layer surface) in a low vacuum environment, and heating the target surface to a temperature which is greater than the threshold temperature for forming an epitaxial layer of the desired material on the target surface in a high vacuum environment (e.g., less than about 1×10^3 Torr, such as less than about 1×10^4 Torr) under otherwise identical conditions. A gas beam containing the buffer layer material and optionally an inert carrier gas is directed at the target surface at a velocity of at least about one meter per second. A conditioning gas is provided in the low vacuum environment. The conditioning gas can be contained in the gas beam, or the conditioning gas can be introduced into the low vacuum environment in a different manner (e.g., leaked into the environment). The conditioning gas can react with species (e.g., contaminants) present at the target surface to remove the species, which can promote the nucleation of the epitaxial buffer layer.

[0079] The epitaxial buffer layer can be grown on a target surface using a low vacuum (e.g., at least about 1×10^3 Torr, at least about 0.1 Torr, or at least about 1 Torr) at a surface temperature below the temperature used to grow the epitaxial layer using physical vapor deposition at a high vacuum (e.g., at most about 1×10^{-4} Torr). The temperature of the target surface can be, for example, from about 25° C. to about 800° C. (e.g., from about 500° C. to about 800° C., or from about 500° C. to about 650° C.).

[0080] The epitaxial layer can be grown at a relatively fast rate, such as, for example, at least about 50 Angstroms per second.

[0081] These methods are described in U.S. Pat. No. 6,027,564, issued Feb. 22, 2000, and entitled "Low Vacuum Process for Producing Epitaxial Layers;" U.S. Pat. No. 6,022,832, issued Feb. 8, 2000, and entitled "Low Vacuum Process for Producing Superconductor Articles with Epitaxial Layers;" and/or commonly owned U.S. patent application Ser. No. 09/007,372, filed Jan. 15, 1998, and entitled "Low Vacuum Process for Producing Epitaxial Layers of Semiconductor Material," all of which are hereby incorporated by reference.

[0082] In some embodiments, an epitaxial buffer layer can be deposited by sputtering from a metal or metal oxide target at a high throughput. Heating of the substrate can be

accomplished by resistive heating or bias and electric potential to obtain an epitaxial morphology. A deposition dwell may be used to form an oxide epitaxial film from a metal or metal oxide target.

[0083] The oxide layer typically present on substrates can be removed by exposure of the substrate surface to energetic ions within a reducing environment, also known as Ion Beam etching. Ion Beam etching can be used to clean the substrate prior to film deposition, by removing residual oxide or impurities from the substrate, and producing an essentially oxide-free preferably biaxially textured substrate surface. This improves the contact between the substrate and subsequently deposited material. Energetic ions can be produced by various ion guns, for example, which accelerate ions such as Ar^+ toward a substrate surface. Preferably, gridded ion sources with beam voltages greater than 150 eV are utilized. Alternatively, a plasma can be established in a region near the substrate surface. Within this region, ions chemically interact with a substrate surface to remove material from that surface, including metal oxides, to produce substantially oxide-free metal surface.

[0084] Another method to remove oxide layers from a substrate is to electrically bias the substrate. If the substrate tape or wire is made negative with respect to the anode potential, it will be subjected to a steady bombardment by ions from the gas prior to the deposition (if the target is shuttered) or during the entire film deposition. This ion bombardment can clean the wire or tape surface of absorbed gases that might otherwise be incorporated in the film and also heat the substrate to elevated deposition temperatures. Such ion bombardment can be further advantageous by improving the density or smoothness of the epitaxial film.

[0085] Upon formation of an appropriately textured, substantially oxide-free substrate surface, deposition of a buffer layer can begin. One or more buffer layers, each including a single metal or oxide layer, can be used. In some preferred embodiments, the substrate is allowed to pass through an apparatus adapted to carry out steps of the deposition method of these embodiments. For example, if the substrate is in the form of a wire or tape, the substrate can be passed linearly from a payout reel to a take-up reel, and steps can be performed on the substrate as it passes between the reels.

[0086] According to some embodiments, substrate materials are heated to elevated temperatures which are less than about 90% of the melting point of the substrate material but greater than the threshold temperature for forming an epitaxial layer of the desired material on the substrate material in a vacuum environment at the predetermined deposition rate. In order to form the appropriate buffer layer crystal structure and buffer layer smoothness, high substrate temperatures are generally preferred. Typical lower limit temperatures for the growth of oxide layers on metal are approximately 200 C. to 800 C., preferably 500 C. to 800 C., and more preferably, 650 C. to 800 C. Various well-known methods such as radiative heating, convection heating, and conduction heating are suitable for short (2 cm to 10 cm) lengths of substrate, but for longer (1 m to 100 m) lengths, these techniques may not be well suited. Also to obtain desired high throughput rates in a manufacturing process, the substrate wire or tape must be moving or transferring between deposition stations during the process. According to particular embodiments, the substrates are heated by resis-

tive heating, that is, by passing a current through the metal substrate, which is easily scaleable to long length manufacturing processes. This approach works well while instantaneously allowing for rapid travel between these zones. Temperature control can be accomplished by using optical pyrometers and closed loop feedback systems to control the power supplied to the substrate being heated. Current can be supplied to the substrate by electrodes which contact the substrate in at least two different segments of the substrate. For example, if the substrate, in the form of a tape or wire, is passed between reels, the reels themselves could act as electrodes. Alternatively, if guides are employed to transfer the substrate between reels, the guides could act as electrodes. The electrodes could also be completely independent of any guides or reels as well. In some preferred embodiments, current is applied to the tape between current wheels.

[0087] In order that the deposition is carried out on tape that is at the appropriate temperature, the metal or oxide material that is deposited onto the tape is desirably deposited in a region between the current wheels. Because the current wheels can be efficient heat sinks and can thus cool the tape in regions proximate to the wheels, material is desirably not deposited in regions proximate to the wheels. In the case of sputtering, the charged material deposited onto the tape is desirably not influenced by other charged surfaces or materials proximate to the sputter flux path. For this reason, the sputter chamber is preferably configured to place components and surfaces which could influence or deflect the sputter flux, including chamber walls, and other deposition elements, in locations distant from the deposition zone so that they do not alter the desired linear flux path and deposition of metal or metal oxide in regions of the tape at the proper deposition temperature.

[0088] More details are provided in commonly owned U.S. patent application Ser. No. 09/500,701, filed on Feb. 9, 2000, and entitled "Oxide Layer Method," and commonly owned U.S. patent application Ser. No. 0/615,669, filed on Jul. 14, 2000, and entitled "Oxide Layer Method," both of which are hereby incorporated by reference in their entirety.

[0089] In preferred embodiments, three buffer layers are used. A layer of Y_2O_3 or CeO_2 (e.g., from about 20 nanometers to about 75 nanometers thick) is deposited (e.g., using electron beam evaporation) onto the substrate surface. A layer of YSZ (e.g., from about 0.20 nanometers about 700 nanometers thick, such as about 75 nanometers thick) is deposited onto the surface of the Y_2O_3 or CeO_2 layer using sputtering (e.g., using magnetron sputtering). A CeO_2 layer (e.g., about 20 nanometers thick) is deposited (e.g., using magnetron sputtering) onto the YSZ surface. The surface of one or more of these layers can be chemically and/or thermally conditioned as described herein.

[0090] In certain embodiments, a buffer layer material can be prepared using solution phase techniques, including metalorganic deposition, which are known to those skilled in the art. Such techniques are disclosed in, for example, S. S. Shoup et al., J. Am. Cer. Soc., Vol. 81, 3019; D. Beach et al., Mat. Res. Soc. Symp. Proc., vol. 495, 263 (1988); M. Paranthaman et al., Superconductor Sci. Tech., vol. 12, 319 (1999); D. J. Lee et al., Japanese J. Appl. Phys., vol. 38, L178 (1999) and M. W. Rupich et al., I.E.E.E. Trans. on Appl. Supercon. vol. 9, 1527.

[0091] In certain embodiments, solution coating processes can be used for deposition of one or a combination of any of

the oxide layers on textured substrates; however, they can be particularly applicable for deposition of the initial (seed) layer on a textured metal substrate. The role of the seed layer is to provide 1) protection of the substrate from oxidation during deposition of the next oxide layer when carried out in an oxidizing atmosphere relative to the substrate (for example, magnetron sputter deposition of yttria-stabilized zirconia from an oxide target); and 2) an epitaxial template for growth of subsequent oxide layers. In order to meet these requirements, the seed layer should grow epitaxially over the entire surface of the metal substrate and be free of any contaminants that may interfere with the deposition of subsequent epitaxial oxide layers.

[0092] In certain embodiments, the buffer layer can be formed using ion beam assisted deposition (IBAD). In this technique, a buffer layer material is evaporated using, for example, electron beam evaporation, sputtering deposition, or pulsed laser deposition while an ion beam (e.g., an argon ion beam) is directed at a smooth amorphous surface of a substrate onto which the evaporated buffer layer material is deposited.

[0093] For example, the buffer layer can be formed by ion beam assisted deposition by evaporating a buffer layer material having a rock-salt like structure (e.g., a material having a rock salt structure, such as an oxide, including MgO, or a nitride) onto a smooth, amorphous surface (e.g., a surface having a root mean square roughness of less than about 100 Angstroms) of a substrate so that the buffer layer material has a surface with substantial alignment (e.g., about 13° or less), both in-plane and out-of-plane.

[0094] The conditions used during deposition of the buffer layer material can include, for example, a substrate temperature of from about 0° C. to about 750° C. (e.g., from about 0° C. to about 400° C., from about room temperature to about 750° C., from about room temperature to about 400° C.), a deposition rate of from about 1.0 Angstrom per second to about 4.4 Angstroms per second, an ion energy of from about 200 eV to about 1200 eV, and/or an ion flux of from about 110 microamperes per square centimeter to about 120 microamperes per square centimeter.

[0095] In some embodiments, when using IBAD, the substrate is formed of a material having a polycrystalline, non-amorphous base structure (e.g., a metal alloy, such as a nickel alloy) with a smooth amorphous surface formed of a different material (e.g., Si₃N₄).

[0096] In certain embodiments, a plurality of buffer layers can be deposited by epitaxial growth on an original IBAD surface. Each buffer layer can have substantial alignment (e.g., about 13° or less), both in-plane and out-of-plane.

[0097] A buffer material can be prepared using solution phase techniques, including metalorganic deposition, such as disclosed in, for example, S. S. Shoup et al., J. Am. Cer. Soc., vol. 81, 3019; D. Beach et al., Mat. Res. Soc. Symp. Proc., vol. 495, 263 (1988); M. Paranthaman et al., Superconductor Sci. Tech., vol. 12, 319 (1999); D. J. Lee et al., Japanese J. Appl. Phys., vol. 38, L178 (1999) and M. W. Rupich et al., I.E.E.E. Trans. on Appl. Supercon. vol. 9, 1527. In certain embodiments, solution coating processes can be used for deposition of one or a combination of any of the oxide layers on textured substrates; however, they can be particularly applicable for deposition of the initial (seed)

layer on a textured metal substrate. The role of the seed layer is to provide 1) protection of the substrate from oxidation during deposition of the next oxide layer when carried out in an oxidizing atmosphere relative to the substrate (for example, magnetron sputter deposition of yttria-stabilized zirconia from an oxide target); and 2) an epitaxial template for growth of subsequent oxide layers. In order to meet these requirements, the seed layer should grow epitaxially over the entire surface of the metal substrate and be free of any contaminants that may interfere with the deposition of subsequent epitaxial oxide layers.

[0098] The formation of oxide buffer layers can be carried out so as to promote wetting of an underlying substrate layer. Additionally, in particular embodiments, the formation of metal oxide layers can be carried out using metal alkoxide or carboxylate precursors (for example, "sol gel" precursors).

Precursor Layer

[0099] Once the textured substrate including buffer layers is prepared, a precursor solution is deposited at a station 630 as described above. As noted above, one or more layers are deposited to form a precursor layer having the desired thickness and overall composition.

[0100] Suitable precursor components include soluble compounds of one or more rare earth elements, one or more alkaline earth metals and one or more transition metals. As used herein, "soluble compounds" of rare earth elements, alkaline earth metals and transition metals refers to compounds of these metals that are capable of dissolving in the solvents contained in the precursor solution. Such compounds include, for example, salts (e.g., nitrates, acetates, alkoxides, halides, sulfates, and trifluoroacetates), oxides and hydroxides of these metals. At least one of the compounds is a fluorine-containing compound, such as the trifluoroacetate.

[0101] Examples of metal salt solutions that can be used are as follows.

[0102] In some embodiments, the metal salt solution can have a relatively small amount of free acid. In aqueous solutions, this can correspond to a metal salt solution with a relatively neutral pH (e.g., neither strongly acidic nor strongly basic). The metal salt solution can be used to prepare multi-layer superconductors using a wide variety of materials that can be used as the underlying layer on which the superconductor layer is formed.

[0103] The total free acid concentration of the metal salt solution can be less than about 1×10^{-3} molar (e.g., less than about 1×10^{-5} molar or about 1×10^{-7} molar). Examples of free acids that can be contained in a metal salt solution include trifluoroacetic acid, acetic acid, nitric acid, sulfuric acid, acids of iodides, acids of bromides and acids of sulfates.

[0104] When the metal salt solution contains water, the precursor composition can have a pH of at least about 3 (e.g., at least about 5 or about 7).

[0105] In some embodiments, the metal salt solution can have a relatively low water content (e.g., less than about 50 volume percent water, less than about 35 volume percent water, less than about 25 volume percent water).

[0106] In general, the rare earth earth metal salt can be any rare earth metal salt that is soluble in the solvent(s) contained in the precursor solution and that, when being processed to form an intermediate (e.g., a metal oxyhalide intermediate), forms rare earth oxide(s) (e.g., Y_2O_3). The rare earth elements may be selected from the group of yttrium, cerium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Typically, the alkaline earth metal is barium, strontium or calcium. Such salts can have, for example, the formula $M(O_2C-(CH_2)_n-CXX'X'')(O_2C-(CH_2)_m-CX''X'''X''''X'''''X''''''X''''''')_2$ or $M(OR)_3$, M is the rare earth metal. n, m and p are each at least one but less than a number that renders the salt insoluble in the solvent(s) (e.g., from one to ten). Each of X, X', X'', X''', X''', X''', X''', X'''' and X'''''' is H, F, Cl, Br or I. R is a carbon containing group, which can be halogenated (e.g., CH_2CF_3) or nonhalogenated. Examples of such salts include nonhalogenated carboxylates, halogenated acetates (e.g., trifluoroacetate, trichloroacetate, tribromoacetate, triiodoacetate), halogenated alkoxides, and nonhalogenated alkoxides. Examples of such nonhalogenated carboxylates include nonhalogenated acetates (e.g., $M(O_2C-CH_3)_3$). Generally, the alkaline earth metal salt can be any alkaline earth metal salt that is soluble in the solvent(s) contained in the precursor solution and that, when being processed to form an intermediate (e.g., a metal oxyhalide intermediate), forms an alkaline earth halide compound (e.g., BaF_2 , $BaCl_2$, $BaBr_2$, BaI_2) prior to forming alkaline earth oxide(s) (e.g., BaO). Such salts can have, for example, the formula $M'(O_2C-(CH_2)_n-CXX'X'')(O_2C-(CH_2)_m-CX''X'''X''''X'''''X''''''X''''''')_2$. M' is the alkaline earth metal. n and m are each at least one but less than a number that renders the salt insoluble in the solvent(s) (e.g., from one to ten). Each of X, x', x'', x''', x''', x''', x''', x'''' and x'''''' is H, F, Cl, B or, I. R can be a halogenated or nonhalogenated carbon containing group. Examples of such salts include halogenated acetates (e.g., trifluoroacetate, trichloroacetate, tribromoacetate, triiodoacetate). Generally, the transition metal is copper. The transition metal salt should be soluble in the solvent(s) contained in the precursor solution. In one or more embodiments of the present invention, the rare earth and the alkaline earth elements can form a metal or mixed metal oxyfluoride in place of or in addition to a rare earth oxide and an alkaline earth fluoride.

[0107] Suitable copper precursor solutions contain a copper salt that is soluble at the appropriate concentration in the solvent(s). Such compounds include copper nitrates, carboxylates, alkoxides, halides, sulfates or trifluoroacetates. Preferably, during conversion of the precursor to the intermediate (e.g., metal oxyhalide), minimal cross-linking occurs between discrete transition metal molecules (e.g., copper molecules). Such transition metals salts can have, for example, the formula $M''(CXX'X''-CO(CH)_aCO-CX'''X''''X''''')(CX'''X''''X''''''X'''''''-CO(CH)_bCO-CX'''X''''X''''''X''''''')$, $M''(O_2C-(CH_2)_n-CXX'X'')$, $(O_2C-(CH_2)_m-CX'''X''''X''''')$ or $M''(OR)_2$. M'' is the transition metal. a and b are each at least one but less than a number that renders the salt insoluble in the solvent(s) (e.g., from one to five). Generally, n and m are each at least one but less than a number that renders the salt insoluble in the solvent(s) (e.g., from one to ten). Each of $X, X', X'', X''', X''', X''''', X''''', X''''', X''''', X''''', X''''', X'''''$ is H, F, Cl Br or I. R is a carbon containing group, which can be

halogenated (e.g., CH_2CF_3) or nonhalogenated. These salts include, for example, nonhalogenated acetates (e.g., $\text{M}^n(\text{O}_2\text{C}-\text{CH}_3)_2$), halogenated acetates, halogenated alkoxides, and nonhalogenated alkoxides. Examples of such salts include copper trichloroacetate, copper tribromoacetate, copper triiodoacetate, $\text{Cu}(\text{CH}_3\text{COCHCOF}_3)_2$, $\text{Cu}(\text{OOCCH}_2\text{H}_5)_2$, $\text{Cu}(\text{CF}_3\text{COCHCOF}_3)_2$, $\text{Cu}(\text{CH}_3\text{COCHCOCH}_3)_2$, $\text{Cu}(\text{CH}_3\text{CH}_2\text{CO}_2\text{CHCOCH}_3)_2$, $\text{CuO}(\text{C}_6\text{H}_5)_2$ and $\text{Cu}_2\text{O}_3\text{Ba}_2(\text{O}-\text{CH}_2\text{CF}_3)_4$. A suitable compound is copper propionate. An example of a nonhalogenated propionate salt of a transition metal is $\text{Cu}(\text{O}_2\text{CC}_2\text{H}_5)_2$. In some embodiments, the transition metal salt is a simple salt, such as copper sulfate, copper nitrate, copper iodide and/or copper oxyate. In some embodiments, n and/or m can have the value zero. In certain embodiments, a and/or b can have the value zero. An illustrative and nonlimiting list of Lewis bases includes nitrogen-containing compounds, such as ammonia and amines. Examples of amines include CH_3CN , $\text{C}_5\text{H}_5\text{N}$ and $\text{R}_1\text{R}_2\text{R}_3\text{N}$. Each of R_1 , R_2 , R_3 is independently H, an alkyl group (e.g., a straight chained alkyl group, a branched alkyl group, an aliphatic alkyl group, a non-aliphatic alkyl group and/or a substituted alkyl group) or the like. Without wishing to be bound by theory, it is believed that the presence of a Lewis base in the metal salt solution can reduce cross-linking of copper during intermediate formation. It is believed that this is achieved because a Lewis base can coordinate (e.g., selective coordinate) with copper ions, thereby reducing the ability of copper to cross-link.

[0108] While the precursor solution typically contains stoichiometric amounts of the component metal compounds, i.e., 3:2:1 Cu:Ba:RE, in some embodiments an excess of copper or a deficiency of barium is used. The ratio of the transition metal to the alkaline earth metal can be greater than 1.5, and the precursor solution can include at least about 5 mol % excess copper, or at least about 20 mol % excess copper.

[0109] In addition to precursor components for the formation of a rare-earth/alkaline-earth-metal/transition-metal oxide, the precursor solution may include additive components and/or dopant components for the formation of flux pinning sites is used in a solution-based method to obtain a superconducting film having pinning centers. The additive compound can be metal compounds, such as soluble compounds of rare earths, alkaline earths or transition metals, cerium, zirconium, silver, aluminum, or magnesium, that form metal oxide or metal in the oxide superconductor film. The precursor solution can provide a dopant metal that partially substitutes for a metal of the precursor component of the precursor solution. Generally, a dopant component can be any metal compound that is soluble in the solvent(s) contained in the precursor solution and that, when processed to form an oxide superconductor, provided a dopant metal that substitutes for an element of the oxide superconductor.

[0110] The solvent or combination of solvents used in the precursor solution can include any solvent or combination of solvents capable of dissolving the metal salts (e.g., metal carboxylate(s)). Such solvents include, for example, alcohols or acids, including methanol, ethanol, isopropanol and butanol, propionic acid or water.

[0111] In embodiments in which the metal salt solution contains trifluoroacetate ion and an alkaline earth metal

cation (e.g., barium), the total amount of trifluoroacetate ion can be selected so that the mole ratio of fluorine contained in the metal salt solution (e.g., in the form of trifluoroacetate) to the alkaline earth metal (e.g., barium ions) contained in the metal salt solution is at least about 2:1 (e.g., from about 2:1 to about 18.5:1, or from about 2:1 to about 10:1).

[0112] The methods of disposing the superconducting composition on the underlying layer (e.g., on a surface of a substrate, such as a substrate having an alloy layer with one or more buffer layers disposed thereon) include spin coating, dip coating, slot coating, web coating and other techniques known in the art.

Decomposition of the Precursor Layer

[0113] At a subsequent station 640, the precursor components are decomposed. The conversion of the precursor components into an oxide superconductor is carried out as has been previously reported for continuous thick precursor films. In the case of precursor components including at least one fluoride-containing salt, the first step of the heating step is performed to decompose the metalorganic molecules to one or more oxyfluoride intermediates of the desired superconductor material.

[0114] An intermediate oxyfluoride film is considered to be any film that is a precursor to a rare earth metal-alkaline earth metal-transition metal oxide superconductor (hereinafter "RE-123") film that is comprised of (1) a mixture of BaF_2 , a rare earth oxide or fluoride and/or transition metal, transition metal oxide or transition metal fluoride, (2) a mixture of a compound comprised of a RE-Ba-O-F phase, a rare earth oxide or fluoride and/or transition metal oxide or fluoride, or (3) as a mixture of a compound comprised of a Ba-O-F phase, rare earth oxides or fluorides and/or transition metal oxide or fluoride. The intermediate film can then be further processed to form a RE-123 oxide superconductor film. The oxide superconductor film also indicates a small, but detectable, fluoride residue.

[0115] Typically, the initial temperature in this step is about room temperature, and the final temperature is from about 190° C. to about 210° C., preferably to a temperature to about 200° C. Preferably, this step is performed using a temperature ramp of at least about 5° C. per minute, more preferably a temperature ramp of at least about 10° C. per minute, and most preferably a temperature ramp of at least about 15° C. per minute. During this step, the partial pressure of water vapor in the nominal gas environment is preferably maintained at from about 5 Torr to about 50 Torr, more preferably at from about 5 Torr to about 30 Torr, and most preferably at from about 20 Torr to about 30 Torr. The partial pressure of oxygen in the nominal gas environment is maintained at from about 0.1 Torr to about 760 Torr and preferably at about 730-740 Torr.

[0116] Heating is then continued to a temperature of from about 200° C. to about 290° C. using a temperature ramp of from about 0.05° C. per minute to about 5° C. per minute (e.g., from about 0.5° C. per minute to about 1° C. per minute). Preferably, the gas environment during this heating step is substantially the same as the nominal gas environment used when the sample is heated to from the initial temperature to from about 190° C. to about 215° C.

[0117] Heating is further continued to a temperature of about 650° C., or more preferably to a temperature of about 400° C., to form the oxyfluoride intermediate. This step is preferably performed using a temperature ramp of at least about 2° C. per minute, more preferably at least about 3° C. per minute, and most preferably at least about 5° C. per minute. Preferably, the gas environment during this heating step is substantially the same as the nominal gas environment used when the sample is heated to from the initial temperature to from about 190° C. to about 215° C.

[0118] In alternate embodiments, barium fluoride is formed by heating the dried solution from an initial temperature (e.g., room temperature) to a temperature of from about 190° C. to about 215° C. (e.g., about 210° C.) in a water vapor pressure of from about 5 Torr to about 50 Torr water vapor (e.g., from about 5 Torr to about 30 Torr water vapor, or from about 10 Torr to about 25 Torr water vapor). The nominal partial pressure of oxygen can be, for example, from about 0.1 Torr to about 760 Torr. In these embodiments, heating is then continued to a temperature of from about 220° C. to about 290° C. (e.g., about 220° C.) in a water vapor pressure of from about 5 Torr to about 50 Torr water vapor (e.g., from about 5 Torr to about 30 Torr water vapor, or from about 10 Torr to about 25 Torr water vapor). The nominal partial pressure of oxygen can be, for example, from about 0.1 Torr to about 760 Torr. This is followed by heating to about 400° C. at a rate of at least about 2° C. per minute (e.g., at least about 3° C. per minute, or at least about 5° C. per minute) in a water vapor pressure of from about 5 Torr to about 50 Torr water vapor (e.g., from about 5 Torr to about 30 Torr water vapor, or from about 10 Torr to about 25 Torr water vapor) to form barium fluoride. The nominal partial pressure of oxygen can be, for example, from about 0.1 Torr to about 760 Torr.

[0119] In certain embodiments, heating the dried solution to form barium fluoride can include putting the coated sample in a pre-heated furnace (e.g., at a temperature of at least about 100° C., at least about 150° C., at least about 200° C., at most about 300° C., at most about 250° C., about 200° C.). The gas environment in the furnace can have, for example, a total gas pressure of about 760 Torr, a predetermined partial pressure of water vapor (e.g. at least about 10 Torr, at least about 15 Torr, at most about 25 Torr, at most about 20 Torr, about 17 Torr) with the balance being molecular oxygen. After the coated sample reaches the furnace temperature, the furnace temperature can be increased (e.g., to at least about 225° C., to at least about 240° C., to at most about 275° C., to at most about 260° C., about 250° C.) at a predetermined temperature ramp rate (e.g., at least about 0.5° C. per minute, at least about 0.75° C. per minute, at most about 2° C. per minute, at most about 1.5° C. per minute, about 1° C. per minute). This step can be performed with the same nominal gas environment used in the first heating step. The temperature of the furnace can then be further increased (e.g., to at least about 350° C., to at least about 375° C., to at most about 450° C., to at most about 425° C., about 450° C.) at a predetermined temperature ramp rate (e.g., at least about 5° C. per minute, at least about 8° C. per minute, at most about 20° C. per minute, at most about 12° C. per minute, about 10° C. per minute). This step can be performed with the same nominal gas environment used in the first heating step.

[0120] The foregoing treatments of a metal salt solution can result in an oxyfluoride intermediate film in which the constituent metal oxides and metal fluorides are homogeneously distributed throughout the film. Preferably, the precursor has a relatively low defect density and is essentially free of cracks through the intermediate thickness. While solution chemistry for barium fluoride formation has been disclosed, other methods can also be used for other precursor solutions.

Patterning the Precursor Layer

[0121] The resultant intermediate films are soft and plastic. They are capable of deformation without brittle material failure. The intermediate films are patterned as described above according to one or more embodiments using a scribing tool at station 645. The scribing tool may be used to pattern a wide continuous web of intermediate film to form material-free gaps where slitting into individual HTS wires or tapes may occur. Alternatively, the scribing tool may be used to form fine filaments for reducing as losses. Both macro and microscale scribing may take place.

Forming the Oxide Superconductor

[0122] The superconductor intermediate film can then be heated to form the desired superconductor layer at a further processing station 650. Typically, this step is performed by heating from about room temperature to a temperature of from about 700° C. to about 825° C., preferably to a temperature of about 740° C. to 800° C. and more preferably to a temperature of about 750° C. to about 790° C., at a temperature ramp of about greater than 25° C. per minute, preferably at a temperature rate of about greater than 100° C. per minute and more preferably at a temperature rate about greater than 200° C. per minute. This step can also start from the final temperature of about 400-650° C. used to form the intermediate oxyfluoride film. During this step, a process gas is flowed over the film surface to supply the gaseous reactants to the film and to remove the gaseous reaction products from the film. The nominal gas environment during this step has a total pressure of about 0.1 Torr to about 760 Torr and is comprised of about 0.09 Torr to about 50 Torr oxygen and about 0.01 Torr to about 150 Torr water vapor and about 0 Torr to about 750 Torr of an inert gas (nitrogen or argon). More preferably, the nominal gas environment has a total pressure of about 0.15 Torr to about 5 Torr and is comprised of about 0.1 Torr to about 1 Torr oxygen and about 0.05 Torr to about 4 Torr water vapor.

[0123] The film is then held at a temperature of about 700° C.-825° C., preferably to a temperature of about 740° C. to 800° C. and more preferably to a temperature of about 750° C. to about 790° C., for a time of about at least 5 minutes to about 120 minutes, preferably for a time of at least about 15 minutes to about 60 minutes, and more preferably for a time of at least about 15 minutes to about 30 minutes. During this step, a process gas is flowed over the film surface to supply the gaseous reactants to the film and to remove the gaseous reaction products from the film. The nominal gas environment during this step has a total pressure of about 0.1 Torr to about 760 Torr and is comprised of about 0.09 Torr to about 50 Torr oxygen and about 0.01 Torr to about 150 Torr water vapor and about 0 Torr to about 750 Torr of an inert gas (nitrogen or argon). More preferably, the nominal gas environment has a total pressure of about 0.15 Torr to about 5 Torr and is comprised of about 0.1 Torr to about 1 Torr oxygen and about 0.05 Torr to about 4 Torr water vapor.

[0124] The film is then cooled to room temperature in a nominal gas environment with an oxygen pressure of about

0.05 Torr to about 150 Torr, preferably about 0.1 Torr to about 0.5 Torr and more preferably from about 0.1 Torr to about 0.2 Torr.

[0125] The resultant superconductor layer is well-ordered (e.g., biaxially textured in plane, or c-axis out of plane and biaxially textured in plane). In embodiments, the bulk of the superconductor material is biaxially textured. A superconductor layer can be at least about one micrometer thick (e.g., at least about two micrometers thick, at least about three micrometers thick, at least about four micrometers thick, at least about five micrometers thick). The oxide superconductor has a c-axis orientation that is substantially constant across its width, the c-axis orientation of the superconductor being substantially perpendicular to the surface of the wire or tape.

Further Processing

[0126] Further processing by noble metal deposition at station 660, oxygen anneal at station 670, lamination at station 680 and slitting at station 690 are carried out. By patterning the oxide superconductor film into thin strips prior to coating with noble metal, the tape is slit into strips of a dimension that is useable in current carrying application without damage to the brittle oxide superconductor film, and which

Incorporation By Reference

[0127] The following documents are hereby incorporated by reference: U.S. Pat. No. 5,231,074, issued on Jul. 27, 1993, and entitled "Preparation of Highly Textured Oxide Superconducting Films from MOD Precursor Solutions;" U.S. Pat. No. 6,022,832, issued Feb. 8, 2000, and entitled "Low Vacuum Process for Producing Superconductor Articles with Epitaxial Layers;" U.S. Pat. No. 6,027,564, issued Feb. 22, 2000, and entitled "Low Vacuum Process for Producing Epitaxial Layers;" U.S. Pat. No. 6,190,752, issued Feb. 20, 2001, and entitled "Thin Films Having Rock-Salt-Like Structure Deposited on Amorphous Surfaces;" U.S. Pat. No. 6,537,689, issued Mar. 25, 2003, and entitled "Multi-Layer Superconductor Having Buffer Layer With Oriented Termination Plane;" PCT Publication No. WO 00/58530, published on Oct. 5, 2000, and entitled "Alloy Materials;" PCT Publication No. WO/58044, published on Oct. 5, 2000, and entitled "Alloy Materials;" PCT Publication No. WO 99/17307, published on Apr. 8, 1999, and entitled "Substrates with Improved Oxidation Resistance;" PCT Publication No. WO 99/16941, published on Apr. 8, 1999, and entitled "Substrates for Superconductors;" PCT Publication No. WO 98/58415, published on Dec. 23, 1998, and entitled "Controlled Conversion of Metal Oxyfluorides into Superconducting Oxides;" PCT Publication No. WO 01/11428, published on Feb. 15, 2001, and entitled "Multi-Layer Articles and Methods of Making Same;" PCT Publication No. WO 01/08232, published on Feb. 1, 2001, and entitled "Multi-Layer Articles And Methods Of Making Same;" PCT Publication No. WO 01/08235, published on Feb. 1, 2001, and entitled "Methods And Compositions For Making A Multi-Layer Article;" PCT Publication No. WO 01/08236, published on Feb. 1, 2001, and entitled "Coated Conductor Thick Film Precursor;" PCT Publication No. WO 01/08169, published on Feb. 1, 2001, and entitled "Coated Conductors With Reduced A. C. Loss;" PCT Publication No. WO 01/15245, published on Mar. 1, 2001, and entitled "Surface Control Alloy Substrates And Methods Of Manufacture Therefore;" PCT Publication No. WO 01/08170, published on Feb. 1, 2001, and entitled "Enhanced Purity Oxide Layer Formation;" PCT Publication No. WO

01/26164, published on Apr. 12, 2001, and entitled "Control of Oxide Layer Reaction Rates;" PCT Publication No. WO 01/26165, published on Apr. 12, 2001, and entitled "Oxide Layer Method;" PCT Publication No. WO 01/08233, published on Feb. 1, 2001, and entitled "Enhanced High Temperature Coated Superconductors;" PCT Publication No. WO 01/08231, published on Feb. 1, 2001, and entitled "Methods of Making A Superconductor;" PCT Publication No. WO 02/35615, published on Apr. 20, 2002, and entitled "Precursor Solutions and Methods of Making Same;" PCT Publication No. WO 2005/121414, published on Dec. 22, 2005, and entitled "Deposition of Buffer Layers on Textured Metal Surfaces;" PCT Publication No. WO 2005/081710, published on Sep. 9, 2005, and entitled "Oxide Films with Nanodot Flux Pinning Sites;" U.S. Pat. No. 6,436,317, issued Aug. 20, 2002, and entitled, "Oxide Bronze Compositions And Textured Articles Manufactured In Accordance Therewith;" U.S. Provisional Patent Application Ser. No. 60/309,116, filed on Jul. 31, 2001, and entitled "Multi-Layer Superconductors And Methods Of Making Same;" U.S. Pat. No. 6,797,313, issued Sep. 28, 2004, and entitled "Superconductor Methods and Reactor;" U.S. Pat. No. 6,669,774, issued Dec. 30, 2003, entitled "Methods and Compositions for Making a Multi-Layer Article;" U.S. Pat. No. 6,974,501, issued Dec. 13, 2005, and entitled "Multi-Layer Articles and Methods of Making Same;" U.S. Pat. No. 6,893,732, issued May 17, 2005, entitled "Multi-Layer Articles and Methods of Making Same;" U.S. Patent publication 2006/0040829, published on Feb. 23, 2006, entitled "propwise Deposition of a Patterned Oxide Superconductor;" U.S. Patent publication 2006/0040830, published on Feb. 3, 2006, entitled "Low AC Loss Filamentary Coated Superconductors;" U.S. Patent publication 2006/0073975, published on Apr. 6, 2006, entitled "Stacked Filamentary Coated Superconductors;" U.S. Patent publication 2006/0073979, published on Apr. 6, 2006, entitled "Architecture for High Temperature Superconductor Wire;" U.S. patent application Ser. No. 11/394,917, filed on Mar. 31, 2006, "Mesh-Type Stabilizer for Filamentary Coated Superconductors" and U.S. Patent publication 2006/0094603, published May 4, 2006, entitled "Thick Superconductor Films with Improved Performance," all of which are hereby incorporated by reference.

What is claimed is:

1. A method for preparing a superconductor article, comprising the steps of:

providing an intermediate metaloxy film on a substrate, the intermediate metaloxy film comprising precursor components to a rare earth-alkaline earth metal-transition metal oxide;

removing selected portions of the intermediate metaloxy fluoride film to obtain a patterned film; and

treating the patterned intermediate film to form a rare earth-alkaline earth metal-transition metal oxide superconductor.

2. The method of claim 1, wherein the intermediate metaloxy film is provided by depositing a precursor solution onto a substrate to form a precursor film, the precursor solution comprising precursor components to a rare earth-alkaline earth metal-transition metal oxide in one or more solvents, and decomposing the precursor film to form an intermediate film comprising the rare earth metal, the alkaline earth metal, and the transition metal.

3. The method of claim 2, wherein the precursor solution comprises a mixture of a rare earth element cation, an alkaline earth metal cation and a transition metal cation.

4. The method of claim 1, wherein the intermediate film is provided by depositing a metaloxy film by e-beam deposition.

5. The method of claim 1, wherein the intermediate film comprises a metal oxyfluoride or a mixture of metal oxides and metal fluorides.

6. The method of claim 1, wherein the patterned film comprises a plurality of regions extending substantially along the length of the article.

7. The method of claim 1, wherein the step of removing selected portions from the intermediate film comprises contacting a tool with the intermediate metaloxy film, the tool having a plurality of scribing surfaces, and removing selected portions of the intermediate film at a contact of the scribing surfaces and the intermediate metaloxy film.

8. The method of claim 7, wherein the plurality of scribing surfaces are positioned on a base to provide scribing surfaces spaced apart at distances commensurate with the width of a high temperature superconductor wire.

9. The method of claim 7, wherein the plurality of scribing surfaces are arranged on a base to provide scribing surfaces spaced apart at distances commensurate with the width of a high temperature superconductor filament.

10. The method of claim 7, wherein the scribing surfaces have a base and a tip, and the tip-to-tip distance is commensurate with the width of a high temperature superconductor wire.

11. The method of claim 7, wherein the scribing surfaces have a base and a tip, and the tip-to-tip distance is commensurate with the width of a high temperature superconductor filament.

12. The method of claim 7, wherein the scribing surfaces have a base and a tip and the tip is rounded.

13. The method of claim 7, wherein the scribing surfaces have a base and a tip and the tip is truncated to increase area contact of the tip with the intermediate film.

14. The method of claim 1, wherein the patterned film comprises a plurality of longitudinally arranged regions having gaps between said regions, said gaps having a width of about 0.1 to about 0.5 mm.

15. The method of claim 1, wherein the patterned intermediate film comprises a filament array comprising a plurality of filaments extending substantially along the length of the substrate and spaced apart from adjacent filaments across the width of the substrate.

16. The method of claim 15, wherein the article comprises about 2 to about 100 filaments and the filaments are about 50 to 1000 μm in width.

17. The method of claim 16, wherein the gap is between 10 and 100 μm .

18. The method of claim 1, further comprising removing scribed material from the patterned film.

19. The method of claim 18, further comprising rinsing the surface of the scribed intermediate metaloxy film to remove scribed material.

20. The method of claim 18, further comprising flowing a gas over the surface of the scribed intermediate metaloxy film to remove scribed material.

21. The method of claim 1, further comprising depositing a protective layer over the patterned oxide superconductor.

22. The method of claim 21, wherein the layer is continuous or discontinuous.

23. The method of claim 21, further comprising cutting the patterned oxide superconductor article along the selected portions to form a plurality of oxide superconductor wires.

24. The method of claim 23, wherein the wires have a width in the range of about 1 mm to 40 mm.

25. The method of claim 6, further comprising cutting the patterned oxide superconductor at a region of the substrate where the intermediate precursor film has been removed to form into two or more wires.

26. The method of claim 1, wherein the overall thickness of the superconductor film is greater than 0.8 μm .

27. The method of claim 15, further comprising depositing a protective layer over the filaments.

28. The method of claim 27, wherein the layer is discontinuous and coats substantially only the filaments.

29. The method of claim 21, further comprising providing a stabilizing layer over the protective layer.

30. The method of claim 29, further comprising cutting the patterned oxidized superconductor along the selected portions to form a plurality of oxide superconductor wires.

31. A method for preparing a superconductor article, comprising the steps of:

depositing an intermediate metaloxy fluoride film on a substrate, the intermediate metaloxy fluoride film comprising precursor components to a rare earth-alkaline earth metal-transition metal oxide, wherein the substrate is at least about 1 mm wide;

removing selected portions of the intermediate metaloxy fluoride film to obtain a patterned film comprising a plurality of longitudinally arranged metaloxy stripes having a width of greater than about 1 mm and gaps between said stripes of about 0.1 to about 0.5 mm; and

treating the patterned intermediate film to form a rare earth-alkaline earth metal-transition metal oxide superconductor.

32. The method of claim 31, wherein the step of removing a plurality of selected regions from the intermediate film comprises a materials removal step selected from the group consisting of mechanical removal, chemical etching, laser etching and physical bombardment.

33. An oxide superconducting tape, comprising:

a biaxially textured substrate greater than 1 cm in width;

a patterned superconducting layer formed on the substrate, wherein said superconducting layer comprises a rare earth barium copper oxide superconductor, the

pattern defining a plurality of parallel stripes of oxide superconductor each having a width of at least 1 mm.

34. The oxide superconducting tape of claim 33, wherein the strip comprises a biaxially oriented substrate and at least one buffer layer comprising a material selected from the group consisting of cerium oxide, lanthanum aluminum oxide, lanthanum manganese oxide, strontium titanium oxide, magnesium oxide, neodymium gadolinium oxide, yttrium oxide and a cerium oxide/yttria-stabilized zirconia.

35. The oxide superconducting tape of claim 33, wherein the strip comprises a biaxially oriented substrate and a biaxially textured buffer layer stack consisting of yttrium oxide, yttria-stabilized zirconium oxide and cerium oxide.

36. The oxide superconducting tape of claim 33, wherein the superconductor film has a thickness greater than 1.0 μm .

37. A metal oxyfluoride tape, comprising:

a biaxially textured substrate greater than 1 cm in width;

a patterned metal oxyfluoride layer deposited on the substrate, wherein said metal oxyfluoride layer comprises a rare earth metal, an alkaline earth metal, and a transition metal of a rare earth barium copper oxide superconductor, the pattern defining a plurality of parallel stripes of metal oxyfluoride each having a width of at least 1 mm.

38. The metal oxyfluoride tape of claim 37, wherein the oxide superconducting stripes have width of about 1-8 mm.

39. A process for preparing a superconductor article, comprising the steps of:

depositing an intermediate metaloxy film onto a substrate, the intermediate metaloxy film comprising precursor components to a rare earth-alkaline earth metal-transition metal oxide in one or more solvents,

passing a scribing tool comprising a plurality of scribing surfaces through the intermediate metaloxy film to selectively remove portions of the intermediate film, wherein a patterned intermediate film is obtained;

treating the patterned intermediate film to form a rare earth-alkaline earth metal-transition metal oxide superconductor;

depositing a protective layer over the patterned oxide superconductor; and

slitting the pattern oxide superconductor along the length of the gap to obtain two or more oxide superconducting wires.

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