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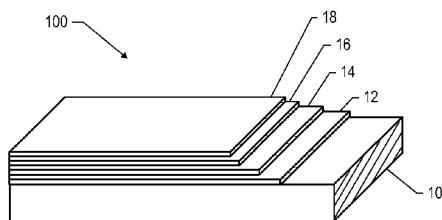
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(54) Title: SUPERCONDUCTING ARTICLE WITH PREFABRICATED NANOSTRUCTURE FOR IMPROVED FLUX PINNING



**FIG. 1**

(57) Abstract: A superconducting article comprises a substrate, a buffer layer overlying the substrate, and a high-temperature superconducting (HTS) layer overlying the buffer layer. The HTS layer includes a plurality of nanorods. A method of forming a superconducting article comprises providing a substrate, depositing a buffer layer overlying the substrate; forming a nanodot array overlying the buffer layer; depositing an array of nanorods nucleated on the nanodot array; and depositing a high-temperature superconducting (HTS) layer around the array of nanorods and overlying the buffer layer.

**WO 2011/017112 A2**

## **SUPERCONDUCTING ARTICLE WITH PREFABRICATED NANOSTRUCTURE FOR IMPROVED FLUX PINNING**

### **STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT**

[0001] Not applicable.

#### Field of the Invention

[0002] The present disclosure generally relates to superconducting articles, and more specifically relates to a superconducting article with prefabricated nanostructure for improved flux pinning.

#### Background of the Invention

[0003] Superconductor materials have long been known and understood by the technical community. Low-temperature superconductors (low- $t_c$  or lts) exhibiting superconducting properties at temperatures requiring use of liquid helium (4.2 k), have been known since 1911. However, it was not until somewhat recently that oxide-based high-temperature (high- $t_c$ ) superconductors have been discovered. Around 1986, a first high-temperature superconductor (HTS), having superconducting properties at a temperature above that of liquid nitrogen (77K) was discovered, namely  $yba_2cu_3o_{7-x}$  (YBCO), followed by development of additional materials over the past 15 years including  $bi_2sr_2ca_2cu_3o_{10+y}$  (BSCCO), and others. The development of high- $t_c$  superconductors has created the potential of economically feasible development of superconductor components and other devices incorporating such materials, due partly to the cost of operating such superconductors with liquid nitrogen rather than the comparatively more expensive cryogenic infrastructure based on liquid helium.

[0004] Of the myriad of potential applications, the industry has sought to develop use of such materials in the power industry, including applications for power generation, transmission, distribution, and storage. In this regard, it is estimated that the inherent resistance of copper-based commercial power components is responsible for billions of dollars per year in losses of electricity, and accordingly, the power industry stands to gain based upon utilization of high-temperature superconductors in power components such as transmission and distribution power cables, generators, transformers, and fault current interrupters/limiters. In addition, other benefits of high-temperature superconductors in the power industry include a factor of 3-10 increase of power-handling capacity, significant reduction in the size (i.e., footprint) and weight of electric power equipment, reduced environmental impact, greater safety, and increased capacity over conventional

technology. While such potential benefits of high-temperature superconductors remain quite compelling, numerous technical challenges continue to exist in the production and commercialization of high-temperature superconductors on a large scale.

[0005] Among the challenges associated with the commercialization of high-temperature superconductors, many exist around the fabrication of a superconducting tape segment that can be utilized for formation of various power components. A first generation of superconducting tape segment includes use of the above-mentioned BSCCO high-temperature superconductor. This material is generally provided in the form of discrete filaments, which are embedded in a matrix of noble metal, typically silver. Although such conductors may be made in extended lengths needed for implementation into the power industry (such as on the order of a kilometer), due to materials and manufacturing costs, such tapes do not represent a widespread commercially feasible product.

[0006] Accordingly, a great deal of interest has been generated in the so-called second-generation HTS tapes that have superior commercial viability. These tapes typically rely on a layered structure, generally including a flexible substrate that provides mechanical support, at least one buffer layer overlying the substrate, the buffer layer optionally containing multiple films, an HTS layer overlying the buffer film, and an optional capping layer overlying the superconductor layer, and/or an optional electrical stabilizer layer overlying the capping layer or around the entire structure. However, to date, numerous engineering and manufacturing challenges remain prior to full commercialization of such second generation-tapes and devices incorporating such tapes.

[0007] Significantly, the critical current of the HTS tape can be strongly affected by the presence of strong magnetic fields. Further, the angle of the magnetic field to the tape significantly affects the critical current. For example, depending on the angle of the magnetic field, the critical current can be reduced by a factor of seven to ten at 1-tesla(t) and 77K compared to the critical current in the absence of a magnetic field. One particular challenge is to reduce the effect of magnetic fields on the critical current of the HTS tape. Additionally, the angular dependence of critical current in the presence of a magnetic field shows a significant anisotropy with a peak in critical current when the field is orientation parallel to the tape and a sharp reduction in critical current as the field is moved away from this orientation. Therefore, another challenge is to improve the critical current in field orientations other than that parallel to the tape. Thus, there remains a need for HTS tapes that have improved performance in strong magnetic fields.

## SUMMARY

[0008] In an embodiment, a superconducting article includes a substrate; a buffer layer overlying the substrate; and a high-temperature superconducting (HTS) layer overlying the buffer layer. The HTS layer can include a plurality of nanorods. In a embodiment, each of the plurality of nanorods can extend at least about 50% of the thickness of the HTS layer. In another embodiment, the nanorods can be substantially parallel to one another. In yet another embodiment, the plurality of nanorods can form an ordered array.

[0009] In another embodiment, a method of forming a superconducting article includes providing a substrate tape, forming a buffer layer overlying the substrate tape, forming a plurality of nanorods, and depositing a high-temperature superconducting (HTS) layer around the plurality of nanorods overlying the buffer layer. In a embodiment, forming the plurality of nanorods can include applying a polymer coating, forming nanoholes through the polymer coating, electrodepositing a metal within the nanoholes to form nanorods, and removing the polymer coating. In another embodiment, forming the plurality of nanorods can include forming a nanoporous layer overlying the buffer layer, electrodepositing a metal into an array of nanopores within the nanoporous layer to form nanorods, and removing the nanoporous layer. In yet another embodiment, forming the plurality of nanorods can include forming a nanodot array overlying the buffer layer and depositing an array of nanorods nucleated by the nanodot array. In a further embodiment, forming the plurality of nanorods can include evaporating nanorod material to form a material cloud, and directing an electron beam through the material cloud towards the substrate tape, thereby depositing an array of nanorods overlying the buffer layer.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The present disclosure may be better understood, and its numerous features and advantages made apparent to those skilled in the art by referencing the accompanying drawings.

[0011] Figure 1 illustrates a prospective view showing the generalized structure of a superconducting article according to an embodiment.

[0012] Figure 2 illustrates an exemplary method of prefabricating nanostructures within a superconducting article.

[0013] Figure 3 shows micrographs of the prefabricated nanostructures according to an embodiment.

[0014] Figure 4 illustrates another exemplary method of prefabricating a nanostructures within a superconducting article.

[0015] Figure 5 shows micrographs of the ZnO nanostructures forming using chemical vapor deposition according to an embodiment.

[0016] Figure 6 shows micrographs of the prefabricated nanostructures according to another embodiment.

[0017] Figure 7 shows micrographs of the self-assembled nanostructures of BZO.

[0018] The use of the same reference symbols in different drawings indicates similar or identical items.

#### DETAILED DESCRIPTION

[0019] Referring now to Figure 1, the generalized layered structure of a superconducting article 100 according to an embodiment of the present invention is depicted. The superconducting article includes a substrate 10, a buffer layer 12 overlying the substrate 10, a superconducting layer 14, followed by a capping layer 16, such as a noble metal, and a stabilizer layer 18, such as a non-noble metal such as copper. The buffer layer 12 may consist of several distinct films. The stabilizer layer 18 may extend around the periphery of the superconducting article 100, thereby encasing it.

[0020] The substrate 10 is generally metal-based, and such as, an alloy of at least two metallic elements. Suitable substrate materials include stainless steel alloys and nickel-based metal alloys such as the known HASTELLOY® or INCONEL® group of alloys. These alloys tend to have desirable creep, chemical and mechanical properties, including coefficient of expansion, tensile strength, yield strength, and elongation. These metals are generally commercially available in the form of spooled tapes, and suitable for superconducting tape fabrication, which will utilize reel-to-reel tape handling.

[0021] The substrate 10 is typically in a tape-like configuration, having a high dimension ratio. As used herein, the term ‘dimension ratio’ is used to denote the ratio of the length of the substrate or tape to the next longest dimension, the width of the substrate or tape. For example, the width of the tape is generally on the order of about 0.1 to about 10 cm, and the length of the tape is at least about 0.1 m; alternatively greater than about 5 m. Superconducting tapes that include substrate 10 may have a length on the order of 100 m or above. Accordingly, the substrate may have a dimension ratio which is fairly high, on the order of not less than 10, not less than about 10<sup>2</sup>, or even not less than about 10<sup>3</sup>. Certain embodiments are longer, having a dimension ratio of 10<sup>4</sup> and higher.

[0022] In one embodiment, the substrate is treated so as to have desirable surface properties for subsequent deposition of the constituent layers of the superconducting tape. For example, the surface may be polished to a desired flatness and surface roughness. Additionally, the substrate may be treated to be biaxially textured as is understood in the

art, such as by the known rabbits (roll assisted biaxially textured substrate) technique, although embodiments herein utilize a non-textured, polycrystalline substrate, such as commercially available nickel-based tapes noted above.

**[0023]** Turning to the buffer layer 12, the buffer layer may be a single layer, or more commonly, be made up of several films. The buffer layer includes a biaxially textured film, having a crystalline texture that is generally aligned along crystal axes both in-plane and out-of-plane of the film. Such biaxial texturing may be accomplished by ion beam assisted deposition (IBAD), a technique that may be advantageously utilized to form a suitably textured buffer layer for subsequent formation of a superconducting layer having desirable crystallographic orientation for superior superconducting properties. Magnesium oxide (MgO) is a typical material of choice for the IBAD film, and may be on the order of about 1 to about 500 nanometers, such as about 5 to about 50 nanometers. Generally, the IBAD film has a rock-salt like crystal structure, as defined and described in us patent 6,190,752, incorporated herein by reference.

**[0024]** The buffer layer may include additional films, such as a barrier film provided to directly contact and be placed in between an IBAD film and the substrate. In this regard, the barrier film may advantageously be formed of an oxide, such as yttria, and functions to isolate the substrate from the IBAD film. A barrier film may also be formed of non-oxides such as silicon nitride. Suitable techniques for deposition of a barrier film include chemical vapor deposition and physical vapor deposition including sputtering. Typical thicknesses of the barrier film may be within a range of about 1 to about 200 nanometers. Still further, the buffer layer may also include an epitaxially grown film(s), formed over the IBAD film. In this context, the epitaxially grown film is effective to increase the thickness of the IBAD film, and may desirably be made principally of the same material utilized for the IBAD layer such as MgO or other compatible materials.

**[0025]** In embodiments utilizing an MgO-based IBAD film and/or epitaxial film, a lattice mismatch between the MgO material and the material of the superconducting layer exists. Accordingly, the buffer layer may further include another buffer film implemented to reduce a mismatch in lattice constants between the superconducting layer and the underlying IBAD film and/or epitaxial film. This buffer film may be formed of materials such as YSZ (yttria-stabilized zirconia), magnesia, ceria, gadolinium zirconium oxide, strontium ruthenate, lanthanum manganate, and generally, perovskite-structured ceramic materials. The buffer film may be deposited by various physical vapor deposition techniques.

**[0026]** While the foregoing has principally focused on implementation of a biaxially textured film in the buffer stack (layer) by a texturing process such as IBAD, alternatively, the substrate surface itself may be biaxially textured. In this case, the buffer layer is generally epitaxially grown on the textured substrate so as to preserve biaxial texturing in the buffer layer. One process for forming a biaxially textured substrate is the process known in the art as RABITS (roll assisted biaxially textured substrates), generally understood in the art.

**[0027]** The superconducting layer 14 is generally in the form of a high-temperature superconductor (HTS) layer. HTS materials are any chosen from any of the high-temperature superconducting materials that exhibit superconducting properties above the temperature of liquid nitrogen, 77k. Such materials may include, for example,  $yba_2cu_3o_{7-x}$ ,  $bi_2sr_2cacu_2o_z$ ,  $bi_2sr_2ca_2cu_3o_{10+y}$ ,  $tl_2ba_2ca_2cu_3o_{10+y}$ , and  $hgb_{a_2}ca_2cu_3o_{8+y}$ . One class of materials includes  $reba_2cu_3o_{7-x}$ , wherein  $0 \geq x > 1$  and  $re$  is a rare earth or combination of rare earth elements. Of the foregoing,  $yba_2cu_3o_{7-x}$ , also generally referred to as YBCO, may be utilized. YBCO may be used with or without the addition of dopants, such as rare earth materials, for example samarium, gadolinium, dysprosium, and holmium. The superconducting layer 14 may be formed by any one of various techniques, including thick and thin film forming techniques. Preferably, a thin film physical vapor deposition technique such as pulsed laser deposition (PLD) can be used for a high deposition rates, or a chemical vapor deposition (CVD) technique can be used for lower cost and larger surface area treatment. The superconducting layer has a thickness on the order of about 0.1 to about 30 microns; alternatively, about 0.5 to about 20 microns, such as about 1 to about 5 microns, in order to get desirable amperage ratings associated with the superconducting layer 14.

**[0028]** In an embodiment, the HTS layer can include a prefabricated nanostructure. The nanostructure can include a plurality of nanorods. The nanorods can serve to pin magnetic flux lines of a magnetic field to reduce the effect of the magnetic field on the critical current of the superconducting article. The nanorods can extend at least about 50% of the thickness of the HTS layer, such as at least about 60% of the thickness of the HTS layer, such as at least about 70% of the thickness of the HTS layer, even at least about 80% of the thickness of the HTS layer. In an embodiment, the nanorods can extend at least about 85% of the thickness of the HTS layer, such as at least about 90% of the thickness of the HTS layer, such as at least about 95% of the thickness of the HTS layer, even at least about 99% of the thickness of the HTS layer.

**[0029]** The nanorods can have a height of between about 0.1 microns and about 10.0 microns, such as between about 1.0 microns and 3.0 microns. Further, the nanorods can have a diameter of between about 0.5 nm and about 100 nm, such as not greater than about 50 nm, even not greater than about 10 nm. In an embodiment, the nanorods can be arranged with an average spacing between adjacent nanorods of between about 0.5 times the diameter and about 100 times the diameter. In another embodiment, the average spacing may be between about 5 nm and about 50 nm. Further, the HTS layer may include not greater than about 30 vol% nanorods.

**[0030]** In an embodiment, the plurality of nanorods may be substantially parallel to one another, that is all of the plurality of nanorods can be oriented in the same direction. Alternatively, at least a portion of the plurality of nanorods may not be parallel to the other nanorods. For example, the plurality of nanorods can include a first portion of nanorods oriented in a first direction and a second portion of nanorods oriented in a second direction.

**[0031]** In an embodiment, the nanorods may be oriented perpendicular to the surface of the substrate. Alternatively, the nanorods may be oriented in a direction other than perpendicular to the substrate, such as at an angle of 45°. The nanorods can be effective at reducing the effect of a magnetic field aligned parallel to the nanorods. In an alternate embodiment, the nanorods may be oriented in random directions. Such a structure may be preferable to achieve improved flux pinning over an entire angular range of magnetic field orientations.

**[0032]** In another embodiment, the plurality of nanorods can be arranged in an ordered array. Generally, an ordered array has a defined spacing between each pair of adjacent nanorods. For example, the nanorods can be arranged in a square array with a substantially constant spacing between adjacent nanorods. Alternatively, the spacing between adjacent nanorods across the width of the tape may be different from the spacing between adjacent nanorods along the length. In an alternate embodiment, the plurality of nanorods can be arranged randomly. Preferably, the density of the nanorods, the number of nanorods per square millimeter, can be similar throughout the HTS layer, even when the spacing between adjacent nanorods is not constant.

**[0033]** The nanorods can consist of a material other than HTS materials. The nanorods can include metal. The metal can be a ferromagnetic metal, such as iron, nickel, or cobalt, or the metal can be a non-ferromagnetic metal such as platinum or gold. Additionally, the nanorods can include ceramic materials, such as  $\text{SnO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,

LaMnO<sub>3</sub> or ZnO. In an embodiment, the nanorods can have a metallic core surround by a ceramic layer.

**[0034]** The superconducting article may also include a capping layer 16 and a stabilizer layer 18, which are generally implemented to provide a low resistance interface and for electrical stabilization to aid in prevention of superconductor burnout in practical use. Further, layers 16 and 18 aid in continued flow of electrical charges along the superconductor in cases where cooling fails or the critical current density is exceeded, and the superconducting layer moves from the superconducting state and becomes resistive. A noble metal is utilized for capping layer 16 to prevent unwanted interaction between the stabilizer layer(s) and the superconducting layer 14. Typical noble metals include gold, silver, platinum, and palladium. Silver is may be used due to its cost and general accessibility. The capping layer 16 may be made be thick enough to prevent unwanted diffusion of the components used in the application of the stabilizer layer 18 into the superconducting layer 14, but is made to be generally thin for cost reasons (raw material and processing costs). Various techniques may be used for deposition of the capping layer 16, including physical vapor deposition, such as dc magnetron sputtering.

**[0035]** The stabilizer layer 18 is generally incorporated to overlie the superconducting layer 14, and overlie and directly contact the capping layer 16 in the embodiment shown in Figure 1. The stabilizer layer 18 functions as a protection/shunt layer to enhance stability against harsh environmental conditions and superconductivity quench. The layer is generally dense and thermally and electrically conductive, and functions to bypass electrical current in case of failure of the superconducting layer or if the critical current of the superconducting layer is exceeded. It may be formed by any one of various thick and thin film forming techniques, such as by laminating a pre-formed copper strip onto the superconducting tape, by using an intermediary bonding material such as a solder. Other techniques have focused on physical vapor deposition, evaporation or sputtering, as well as wet chemical processing such as electro-less plating, and electroplating. In this regard, the capping layer 16 may function as a seed layer for deposition of copper thereon. Notably, the capping layer 16 and the stabilizer layer 18 may be altered or not used.

**[0036]** Turning to the process of prefabricating the nanostructure, various techniques can be used to prefabricate the nanostructure. In one embodiment, high-energy particles can be utilized to form a plurality of randomly distributed nanoholes which can be used to form nanorods. Figure 2 illustrates an exemplary method of forming an HTS layer having a plurality of randomly distributed nanorods. At 202, a tape 204 can be provided.

The tape can include substrate and buffer layers 206 and a conducting layer 208 overlying the substrate and buffer layers 206. The conducting layer 208 can be a thin nickel layer. At 210, a polymer layer 212, such as a polycarbonate film, can be deposited overtop the conducting layer 208, such as by spin coating or other coating techniques known in the art. At 214, the polymer layer 212 can be irradiated with an ion beam, creating damage tracks 216 within the polymer layer 212. When passing through the polymer layer 212, high-energy particles can create a core of low molecular weight material along their path. Altering the duration of exposure and/or the intensity of the ion beam can control the number of damage tracks per mm<sup>2</sup>. In addition, altering the direction of bombardment of the ion beam can create nanoholes at multiple orientations. Consequently, nanorods aligned at different orientations could be created which can result in improved flux pinning over a wide angular range of magnetic field orientations.

[0037] At 218, the polymer layer 212 can be exposed to uv radiation to further develop the damage tracks 216 within the polymer layer 212. At 220, the polymer layer 212 can be etched to form nanoholes 222 corresponding to the damage tracks 216 within the polymer layer 212. The etching chemicals can preferentially attack the damage tracks 216, removing the low molecular weight materials faster than the rest of the polymer layer 212. Altering the duration of etching can control the diameter of the nanoholes. The nanoholes 222 can extend through the polymer layer 212 to the conducting layer 208. Figure 3a shows a micrograph of the nanoholes formed through the polymer layer 212.

[0038] Returning to Figure 2 at 224, metal, such as nickel or gold, can be electroplated within the nanoholes 222 to form nanorods 226 extending from the conducting layer 208 through the polymer layer 212. At 228, the polymer layer 212 can be exposed to an additional etching process to completely remove the remaining polymer layer 212, leaving the nanorods 226 intact. Figure 3b and Figure 3c show micrographs of nanorods. Returning to Figure 2 at 236, HTS material can be deposited to form an HTS layer surrounding the nanorods 226. The HTS material can be deposited using one of the various techniques known in the art, including PLD, CVD, spray pyrolysis, and the like.

[0039] In an embodiment, the conducting layer can be oxidized, such as to form nickel oxide, prior to the deposition of the HTS material. Additionally, a layer of lamno<sub>3</sub> may be deposited overtop the nickel oxide prior to the deposition of the HTS material.

[0040] In a second embodiment, nanorods can be formed using a nanoporous template. Figure 4 illustrates an exemplary process of using nanoporous templates to form a prefabricated nanostructure with the HTS layer. At 402, a substrate 404 and a buffer

layer 406 are provided. Additionally, an aluminum layer 408 is deposited overtop the buffer layer 406. For example, the aluminum layer can be deposited by sputtering or thermal evaporation. At 410, an anodic oxidation process can convert the aluminum layer 408 into an anodized aluminum oxide layer 412 including a highly ordered array of nanopores 414. At 416, metal, such as nickel or gold, can be electrodeposited within the nanopores 414 forming nanorods 418. At 420, the aluminum oxide layer 412 is removed by etching, leaving the nanorods 418 attached to the buffer layer 406. At 424, HTS material can be deposited to form an HTS layer 426 surrounding the nanorods 418. The HTS material can be deposited using one of the various techniques known in the art, including PLD, CVD, spray pyrolysis, and the like.

**[0041]** Alternatively, other inorganic nanotemplates can be used during the process of forming the nanorods. For example, aluminum and silicon can be sputtered onto the buffer layer to form aluminum nanorods embedded within a silicon matrix. The aluminum can be preferentially etched leaving nanopores within the silicon matrix.

**[0042]** In a third embodiment, chemical vapor deposition or chemical solution deposition can be used to form nanorods on predefined nucleation sites. For example, a nanodot array using materials such as colloidal gold particles or similar material can be deposited on the buffer surface as a nucleation site for the nanorods. Vapor-solid-liquid phase growth can be employed to grow the nanorods using the nanodots as a nucleation site. For example, ZnO can be mixed with graphite and vaporized. The vaporized material can be deposited on the nanodot templates. The spacing and density of the nanorods can depend on the spacing and density of the nanodots. The diameter and length of the nanorods can depend on the vaporization temperature and time and the deposition temperature and time. Other materials such as magnetic oxides can be used to form the nanorods that could lead to ferromagnetic pinning. Further, HTS material can be deposited around the nanorods to form an HTS layer embedding the nanorods. Since the nanorods are formed without the need for a nanoporous mask or template, no etching process may be needed to remove the mask or template from the buffer surface after the growth of the nanorods. Accordingly, the CVD nanorod deposition can be performed in an upstream portion of a CVD reactor used for depositing the HTS layer.

**[0043]** Figures 5a-5c show micrographs of the ZnO nanostructures formed by CVD. Figures 5a and 5b show a faceted, plate-like nanostructure formed without the use of gold nanodots. Figure 5c shows ZnO nanorods formed on a buffered template on a flexible metal substrate using CVD.

**[0044]** In yet another embodiment, nanorods can be formed using a high energy, focused electron beam. The tape, including the substrate and the buffer layers, can be within a vacuum chamber. The nanorod material can be evaporated into the atmosphere surrounding the substrate. An electron beam can be focused on the surface of the buffer layer, forcing any nanorod material crossing the path of the electron beam to be deposited on the buffer layer. The electron beam can be focused to a spot on the order of a few nanometers, resulting in the deposition of nanorods having a diameter of a few nanometers. Modifying the electron beam size, current density, concentration of nanorod material, and exposure time can control the length and diameter of the nanorods. Various patterns of nanorods can be formed by moving the focal point of the electron beam across the surface of the buffer layer, allowing the density and separation of the nanorods to be easily controlled. Figures 6a-6c show micrographs of the platinum nanorods formed using a focused electron beam. Figure 6a shows the nanorod array from above and Figure 6b shows the nanorod array in a 52° inclined view. Figure 6c shows a single nanorod of the array having a diameter of about 100 nm and a length of about 600 nm.

**[0045]** In an embodiment, the nanorods can be formed from or coated with an oxides compatible with the HTS material and the HTS material fabrication. The oxide, such as  $\text{LaMnO}_3$ , can prevent a metal core from reacting with the HTS material during high temperature processing, preventing degradation of the transition temperature of the HTS material. Additionally, the oxide layer can match the lattice properties of the HTS layer, reducing lattice mismatch effects.

**[0046]** Alternatively, the nanorods can induce strain in the interface between the HTS layer and the nanorods, resulting in additional pinning. For example, magnetic pinning can be accomplished using ferromagnetic nanorods surrounded by metal oxide nanotubes. The nanotubes can prevent the ferromagnetic material, such as iron or nickel, from interacting with the HTS material. Additionally, the nanotubes can have a lattice mismatch, structural mismatch, or a thermal expansion coefficient mismatch with the HTS material, thus inducing interfacial strain between the HTS material and the nanotube. The interfacial strain can act to further pin magnetic field lines. For example, the nanotubes can be formed from  $\text{ZnO}$  which has a hexagonal structure, compared to the orthorhombic perovskite structure of an HTS material such as YBCO.

**[0047]** In another embodiment, the spacing of the nanorods can be selected to correspond to the strength of an applied magnetic field. The density of the nanorods can be chosen to match the density of the magnetic flux lines. For example, a superconducting article for

use in a 1 t field can have a spacing of about 40 nm between adjacent nanorods, a superconducting article for use in a 5 t magnetic field can have a spacing of about 20 nm between adjacent nanorods, and a superconducting article for use in a 15 t field can have a spacing of about 10 nm between adjacent nanorods.

**[0048]** In another embodiment, the plurality of nanorods can include a first subset of nanorods and a second subset of nanorods. The second subset of nanorods can be interspersed among the first subset of nanorods. Additionally, the second subset of nanorods may have a different orientation a different spacing, different diameter, different height, a different material, or any combination thereof compared to the first subset of nanorods. For example, the first subset of nanorods can oriented to extend vertically from the surface of the buffer layer and the second subset of nanorods can be oriented at a 45° angle from the surface of the buffer layer.

**[0049]** Having formed the nanostructure, the HTS material can be deposited overtop the buffer layer and surrounding the nanorods. The HTS material may be deposited using a variety of techniques known in the art, including PLD, CVD, MOCVD (metal-organic CVD), and spray pyrolysis. Deposition techniques such as PLD and MOCVD that can deposit a superconductor layer relatively high rate. For example, MOCVD can be used to deposit HTS material at a rate of at least about 5 microns per hour, such as at least about 10 microns per hour, even at least about 30 microns per hour. Due to the prefabrication of the nanorods, changes to the deposition process can be minimized, including maintaining the deposition at a relative high rate. Further, during deposition of the HTS layer, a long length substrate can be translated through a deposition zone at a rate of at least about 10 meters per hour, such as at least about 30 meters per hour, even at least about 50 meters per hour.

**[0050]** Prior attempts at pinning magnetic fields have included creating defects in the HTS material using heavy ion radiation. However, heavy ion radiation may not be practical during large-scale manufacturing. More recently, attempts have been made to dope the HTS material with bazro<sub>3</sub> (BZO) or basno<sub>3</sub> (BSO). The BZO or BSO inclusions can self assemble during deposition of the HTS layer to form nano-scale columns, as shown in Figure 7. As can be seen in Figure 7, individual self-assembled nanoscale columns generally do not extend substantially the entire thickness of the HTS layer, nor are they attached to the buffer layer. Rather, the self-assembled nano-columns nucleate at apparently random depths and extend for varying lengths. It has been found

that the self-assembly of the nanostructures can be sensitive to the deposition rate, and requires a significantly lower rate of deposition of the HTS layer.

**[0051]** At least one embodiment is disclosed and variations, combinations, and/or modifications of the embodiment(s) and/or features of the embodiment(s) made by a person having ordinary skill in the art are within the scope of the disclosure. Alternative embodiments that result from combining, integrating, and/or omitting features of the embodiment(s) are also within the scope of the disclosure. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g., from about 1 to about 10 includes, 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, etc.). For example, whenever a numerical range with a lower limit,  $r_l$ , and an upper limit,  $r_u$ , is disclosed, any number falling within the range is specifically disclosed. In particular, the following numbers within the range are specifically disclosed:  $r=r_l + k * (r_u - r_l)$ , wherein  $k$  is a variable ranging from 1 percent to 100 percent with a 1 percent increment, i.e.,  $k$  is 1 percent, 2 percent, 3 percent, 4 percent, 5 percent, .... 50 percent, 51 percent, 52 percent... 95 percent, 96 percent, 97 percent, 98 percent, 99 percent, or 100 percent. Moreover, any numerical range defined by two  $r$  numbers as defined in the above is also specifically disclosed. Use of the term "optionally" with respect to any element of a claim means that the element is required, or alternatively, the element is not required, both alternatives being within the scope of the claim. Use of broader terms such as comprises, includes, and having should be understood to provide support for narrower terms such as consisting of, consisting essentially of, and comprised substantially of. Accordingly, the scope of protection is not limited by the description set out above but is defined by the claims that follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated as further disclosure into the specification and the claims are embodiment(s) of the present invention. The discussion of a reference in the disclosure is not an admission that it is prior art, especially any reference that has a publication date after the priority date of this application. The disclosure of all patents, patent applications, and publications cited in the disclosure are hereby incorporated by reference, to the extent that they provide exemplary, procedural or other details supplementary to the disclosure.

## CLAIMS

We Claim:

1. A superconducting article comprising:
  - a substrate;
  - a buffer layer overlying the substrate; and
  - a high-temperature superconducting (HTS) layer overlying the buffer layer, the HTS layer including a plurality of nanorods, each of the plurality of nanorods extending at least about 50% of the thickness of the HTS layer.
2. The superconducting article of claim 1, wherein each of the nanorods extends at least about 60% of the thickness of the HTS layer.
3. The superconducting article of claim 2, wherein each of the nanorods extends at least about 70% of the thickness of the HTS layer.
4. The superconducting article of claim 3, wherein each of the nanorods extends at least about 80% of the thickness of the HTS layer.
5. The superconducting article of claim 4, wherein each of the nanorods extends at least about 85% of the thickness of the HTS layer.
6. The superconducting article of claim 5, wherein each of the nanorods extends at least about 90% of the thickness of the HTS layer.
7. The superconducting article of claim 6, wherein each of the nanorods extends at least about 95% of the thickness of the HTS layer.
8. The superconducting article of claim 7, wherein each of the nanorods extends at least about 99% of the thickness of the HTS layer.
9. The superconducting article of claim 1, wherein the HTS layer further includes a HTS material, the plurality of nanorods include a material distinct from the HTS material.

10. The superconducting article of claim 1, wherein the HTS layer further includes a HTS material, the plurality of nanorods include a material distinct from the HTS material.
11. The superconducting article of claim 10, wherein the HTS material includes  $reba_2cu_3o_{7-x}$ , wherein  $0 \geq x > 1$  and  $re$  is a rare earth or combination of rare earth elements.
12. The superconducting article of claim 11, wherein the HTS material includes  $yba_2cu_3o_{7-x}$ .
13. The superconducting article of claim 1, wherein the nanorods include a metal, a metal oxide, or any combination thereof.
14. The superconducting article of claim 1, wherein each of the plurality of nanorods are fixed to the buffer layer.
15. The superconducting article of claim 1, wherein the plurality of nanorods are predominantly aligned perpendicular to the buffer surface.
16. The superconducting article of claim 1, wherein the plurality of nanorods are randomly oriented with respect to the buffer surface.
17. The superconducting article of claim 1, wherein the plurality of nanorods are predominantly aligned at an angle other than perpendicular to the buffer surface.
18. The superconducting article of claim 1, wherein each nanorod has a diameter of between about 0.5 nm and about 100 nm.
19. The superconducting article of claim 18, wherein the diameter is not greater than about 50 nm.
20. The superconducting article of claim 19, wherein the diameter is not greater than about 10 nm.

21. The superconducting article of claim 18, wherein the spacing between an adjacent pair of nanorods is between about 0.5 times the diameter of the nanorods and about 100 times the diameter of the nanorods.
22. The superconducting article of claim 1, wherein the spacing between an adjacent pair of nanorods is between about 5 nm and about 50 nm.
23. The superconducting article of claim 1, wherein each nanorod has a height of between about 0.1 microns and about 10.0 microns.
24. The superconducting article of claim 23, wherein the height is between about 1.0 micron and about 3.0 microns.
25. The superconducting article of claim 1, wherein the HTS layer includes not greater than about 30 vol% nanorods.
26. The superconducting article of claim 1, wherein the plurality of nanorods includes a first set of nanorods and a second set of nanorods,
27. The superconducting article of claim 26, wherein the first set of nanorods are oriented substantially parallel with one another and the second set of nanorods are oriented substantially parallel with one another.
28. The superconducting article of claim 26, wherein the first set of nanorods and the second set of nanorods are oriented in substantially different directions.
29. The superconducting article of claim 26, wherein the first set of nanorods have a first diameter and the second set of nanorods has a second diameter.
30. The superconducting article of claim 26, wherein the first set of nanorods have a first spacing and the second set of nanorods has a second spacing.

31. A superconducting article comprising:
  - a substrate;
  - a buffer layer overlying the substrate; and
  - a high-temperature superconducting (HTS) layer overlying the buffer layer, the HTS layer including a plurality of nanorods, the nanorods are fixed to the buffer layer.
32. The superconducting article of claim 31, wherein the HTS layer further includes a HTS material, the plurality of nanorods include a material distinct from the HTS material.
33. The superconducting article of claim 31, wherein the nanorods include a metal, a metal oxide, or any combination thereof.
34. The superconducting article of claim 31, wherein nanorods are substantially parallel to one another.
35. The superconducting article of claim 34, wherein the plurality of nanorods are predominantly aligned perpendicular to the buffer surface.
36. The superconducting article of claim 34, wherein the plurality of nanorods are predominantly aligned at an angle other than perpendicular to the buffer surface.
37. The superconducting article of claim 31, wherein the plurality of nanorods are randomly oriented with respect to the buffer surface.
38. The superconducting article of claim 31, wherein each nanorod has a diameter of between about 0.5 nm and about 100 nm.
39. The superconducting article of claim 38, wherein the spacing between an adjacent pair of nanorods is between about 0.5 times the diameter of the nanorods and about 100 times the diameter of the nanorods.
40. The superconducting article of claim 31, wherein the spacing between an adjacent pair of nanorods is between about 5 nm and about 50 nm.

41. The superconducting article of claim 31, wherein each nanorod has a height of between about 0.1 microns and about 10.0 microns.
42. The superconducting article of claim 31, wherein the HTS layer includes not greater than about 30 vol% nanorods.
43. A superconducting article comprising:
  - a substrate;
  - a buffer layer overlying the substrate; and
  - a high-temperature superconducting (HTS) layer overlying the buffer layer, the HTS layer including a plurality of nanorods, the plurality of nanorods form an ordered array.
44. The superconducting article of claim 43, wherein the HTS layer further includes a HTS material, the plurality of nanorods include a material distinct from the HTS material.
45. The superconducting article of claim 43, wherein the nanorods include a metal, a metal oxide, or any combination thereof.
46. The superconducting article of claim 43, wherein each nanorod is fixed to the buffer layer.
47. The superconducting article of claim 43, wherein the plurality of nanorods are predominantly aligned perpendicular to the buffer surface.
48. The superconducting article of claim 43, wherein the plurality of nanorods are predominantly aligned at an angle other than perpendicular to the buffer surface.
49. The superconducting article of claim 43, wherein the plurality of nanorods are randomly oriented with respect to the buffer surface.
50. The superconducting article of claim 43, wherein each nanorod has a diameter of between about 0.5 nm and about 100 nm.

51. The superconducting article of claim 50, wherein the spacing between an adjacent pair of nanorods is between about 0.5 times the diameter of the nanorods and about 100 times the diameter of the nanorods.
52. The superconducting article of claim 43, wherein the spacing between an adjacent pair of nanorods is between about 5 nm and about 50 nm.
53. The superconducting article of claim 43, wherein each nanorod has a height of between about 0.1 microns and about 10.0 microns.
54. The superconducting article of claim 43, wherein the HTS layer includes not greater than about 30 vol% nanorods.
55. A method of forming a superconducting article comprising:
  - providing a substrate tape;
  - forming a buffer layer overlying the substrate tape;
  - forming a plurality of nanorods; and
  - depositing a high-temperature superconducting (HTS) layer around the plurality of nanorods overlying the buffer layer.
56. The method of claim 55, wherein depositing occurs at a rate of at least about 5 microns per hour.
57. The method of claim 56, wherein depositing occurs at a rate of at least about 10 microns per hour.
58. The method of claim 57, wherein depositing occurs at a rate of at least about 30 microns per hour.
59. The method of claim 55, further including translating the substrate tape through a deposition zone during depositing the high-temperature superconducting (HTS) layer.
60. The method of claim 59, wherein translating occurs at a rate of at least about 10 meters per hour.

61. The method of claim 60, wherein translating occurs at a rate of at least about 30 meters per hour.
62. The method of claim 61, wherein translating occurs at a rate of at least about 50 meters per hour.
63. The method of claim 55, wherein the HTS layer includes a HTS material, the plurality of nanorods include a material distinct from the HTS material.
64. The method of claim 63, wherein the HTS material includes  $reba_2cu_3o_{7-x}$ , wherein  $0 \geq x > 1$  and re is a rare earth or combination of rare earth elements.
65. The method of claim 64, wherein the HTS material includes  $yba_2cu_3o_{7-x}$ .
66. The method of claim 55, wherein each of the plurality of nanorods include a metal, a metal oxide, or any combination thereof.
67. The method of claim 55, wherein each nanorod is fixed to the buffer layer.
68. The method of claim 55, wherein the plurality of nanorods are predominantly aligned perpendicular to the buffer surface.
69. The method of claim 55, wherein the plurality of nanorods are predominantly aligned at an angle other than perpendicular to the buffer surface.
70. The method of claim 55, wherein the plurality of nanorods are randomly oriented with respect to the buffer surface.
71. The method of claim 55, wherein each nanorod has a diameter of between about 0.5 nm and about 100 nm.
72. The method of claim 71, wherein the spacing between an adjacent pair of nanorods is between about 0.5 times the diameter of the nanorods and about 100 times the diameter of the nanorods.

73. The method of claim 55, wherein the spacing between an adjacent pair of nanorods is between about 5 nm and about 50 nm.
74. The method of claim 55, wherein each nanorod has a height of between about 0.1 microns and about 10.0 microns.
75. The method of claim 55, wherein the HTS layer includes not greater than about 30 vol% nanorods.
76. A method of forming a superconducting article comprising:
  - providing a substrate tape;
  - forming a buffer layer overlying the substrate tape;
  - applying a polymer coating;
  - forming nanoholes through the polymer coating;
  - electrodepositing a metal into the nanoholes to form a plurality of nanorods;
  - removing the polymer coating; and
  - depositing a high-temperature superconducting (HTS) layer around the plurality of nanorods overlying the buffer layer.
77. The method of claim 76, wherein depositing occurs at a rate of at least about 5 microns per hour.
78. The method of claim 76, further including translating the substrate tape through a deposition zone during depositing the high-temperature superconducting (HTS) layer.
79. The method of claim 78, wherein translating occurs at a rate of at least about 10 meters per hour.
80. The method of claim 76, wherein the HTS layer includes a HTS material, the plurality of nanorods include a material distinct from the HTS material.
81. The method of claim 76, wherein the nanorods include a metal, a metal oxide, or any combination thereof.

82. The method of claim 76, wherein each nanorod is fixed to the buffer layer.
83. The method of claim 76, wherein the plurality of nanorods are predominantly aligned perpendicular to the buffer surface.
84. The method of claim 76, wherein the plurality of nanorods are predominantly aligned at an angle other than perpendicular to the buffer surface.
85. The method of claim 76, wherein the plurality of nanorods are randomly oriented with respect to the buffer surface.
86. The method of claim 76, wherein each nanorod has a diameter of between about 0.5 nm and about 100 nm.
87. The method of claim 86, wherein the spacing between an adjacent pair of nanorods is between about 0.5 times the diameter of the nanorods and about 100 times the diameter of the nanorods.
88. The method of claim 76, wherein the spacing between an adjacent pair of nanorods is between about 5 nm and about 50 nm.
89. The method of claim 76, wherein each nanorod has a height of between about 0.1 microns and about 10.0 microns.
90. The method of claim 76, wherein the HTS layer includes not greater than about 30 vol% nanorods.

91. A method of forming a superconducting article comprising:
  - providing a substrate tape;
  - depositing a buffer layer overlying the substrate tape;
  - forming a nanoporous layer overlying the buffer layer, the nanoporous layer having an array of nanopores;
  - electrodepositing a metal into the array of nanopores to form an array of nanorods;
  - removing the nanoporous layer; and
  - depositing a high-temperature superconducting (HTS) layer around the array of nanorods and overlying the buffer layer.
92. The method of claim 91, wherein depositing occurs at a rate of at least about 5 microns per hour.
93. The method of claim 91, further including translating the substrate tape through a deposition zone during depositing the high-temperature superconducting (HTS) layer.
94. The method of claim 93, wherein translating occurs at a rate of at least about 10 meters per hour.
95. The method of claim 91, wherein the HTS layer includes a HTS material, the plurality of nanorods include a material distinct from the HTS material.
96. The method of claim 91, wherein the nanorods include a metal, a metal oxide, or any combination thereof.
97. The method of claim 91, wherein each nanorod is fixed to the buffer layer.
98. The method of claim 91, wherein the plurality of nanorods are predominantly aligned perpendicular to the buffer surface.
99. The method of claim 91, wherein the plurality of nanorods are predominantly aligned at an angle other than perpendicular to the buffer surface.

100. The method of claim 91, wherein the plurality of nanorods are randomly oriented with respect to the buffer surface.

101. The method of claim 91, wherein each nanorod has a diameter of between about 0.5 nm and about 100 nm.

102. The method of claim 101, wherein the spacing between an adjacent pair of nanorods is between about 0.5 times the diameter of the nanorods and about 100 times the diameter of the nanorods.

103. The method of claim 91, wherein the spacing between an adjacent pair of nanorods is between about 5 nm and about 50 nm.

104. The method of claim 91, wherein each nanorod has a height of between about 0.1 microns and about 10.0 microns.

105. The method of claim 91, wherein the HTS layer includes not greater than about 30 vol% nanorods.

106. A method of forming a superconducting article comprising:

providing a substrate tape;

depositing a buffer layer overlying the substrate tape;

forming a nanodot array overlying the buffer layer;

depositing an array of nanorods nucleated on the nanodot array; and

depositing a high-temperature superconducting (HTS) layer around the array of nanorods and overlying the buffer layer.

107. The method of claim 106, wherein depositing of the HTS layer occurs at a rate of at least about 5 microns per hour.

108. The method of claim 106, further including translating the substrate tape through a deposition zone during depositing the high-temperature superconducting (HTS) layer.

109. The method of claim 108, wherein translating occurs at a rate of at least about 10 meters per hour.

110. The method of claim 106, wherein the HTS layer includes a HTS material, the plurality of nanorods include a material distinct from the HTS material.

111. The method of claim 106, wherein the nanorods include a metal, a metal oxide, or any combination thereof.

112. The method of claim 106, wherein each nanorod is fixed to the buffer layer.

113. The method of claim 106, wherein the plurality of nanorods are predominantly aligned perpendicular to the buffer surface.

114. The method of claim 106, wherein each nanorod has a diameter of between about 0.5 nm and about 100 nm.

115. The method of claim 114, wherein the spacing between an adjacent pair of nanorods is between about 0.5 times the diameter of the nanorods and about 100 times the diameter of the nanorods.

116. The method of claim 106, wherein the spacing between an adjacent pair of nanorods is between about 5 nm and about 50 nm.

117. The method of claim 106, wherein each nanorod has a height of between about 0.1 microns and about 10.0 microns.

118. The method of claim 106, wherein the HTS layer includes not greater than about 30 vol% nanorods.

119. A method of forming a superconducting article comprising:
  - providing a substrate tape;
  - depositing a buffer layer overlying the substrate tape;
  - evaporating a nanorod material to form a material cloud;
  - directing an electron beam through the material cloud towards the substrate tape, thereby depositing an array of nanorods overlying the buffer layer; and
  - depositing a high-temperature superconducting (HTS) layer around the array of nanorods and overlying the buffer layer.
120. The method of claim 119, wherein depositing occurs at a rate of at least about 5 microns per hour.
121. The method of claim 119, further including translating the substrate tape through a deposition zone during depositing the high-temperature superconducting (HTS) layer.
122. The method of claim 121, wherein translating occurs at a rate of at least about 10 meters per hour.
123. The method of claim 119, wherein the HTS layer includes a HTS material, the plurality of nanorods include a material distinct from the HTS material.
124. The method of claim 119, wherein the nanorods include a metal, a metal oxide, or any combination thereof.
125. The method of claim 119, wherein each nanorod is fixed to the buffer layer.
126. The method of claim 119, wherein the plurality of nanorods are predominantly aligned perpendicular to the buffer surface.
127. The method of claim 119, wherein the plurality of nanorods are predominantly aligned at an angle other than perpendicular to the buffer surface.
128. The method of claim 119, wherein the plurality of nanorods are randomly oriented with respect to the buffer surface.

129. The method of claim 119, wherein each nanorod has a diameter of between about 0.5 nm and about 100 nm.

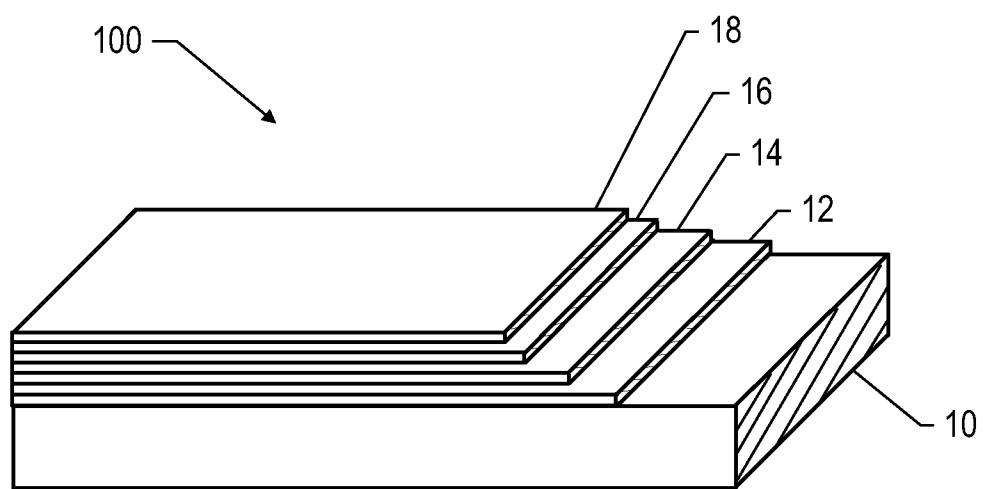
130. The method of claim 129, wherein the spacing between an adjacent pair of nanorods is between about 0.5 times the diameter of the nanorods and about 100 times the diameter of the nanorods.

131. The method of claim 119, wherein the spacing between an adjacent pair of nanorods is between about 5 nm and about 50 nm.

132. The method of claim 119, wherein each nanorod has a height of between about 0.1 microns and about 10.0 microns.

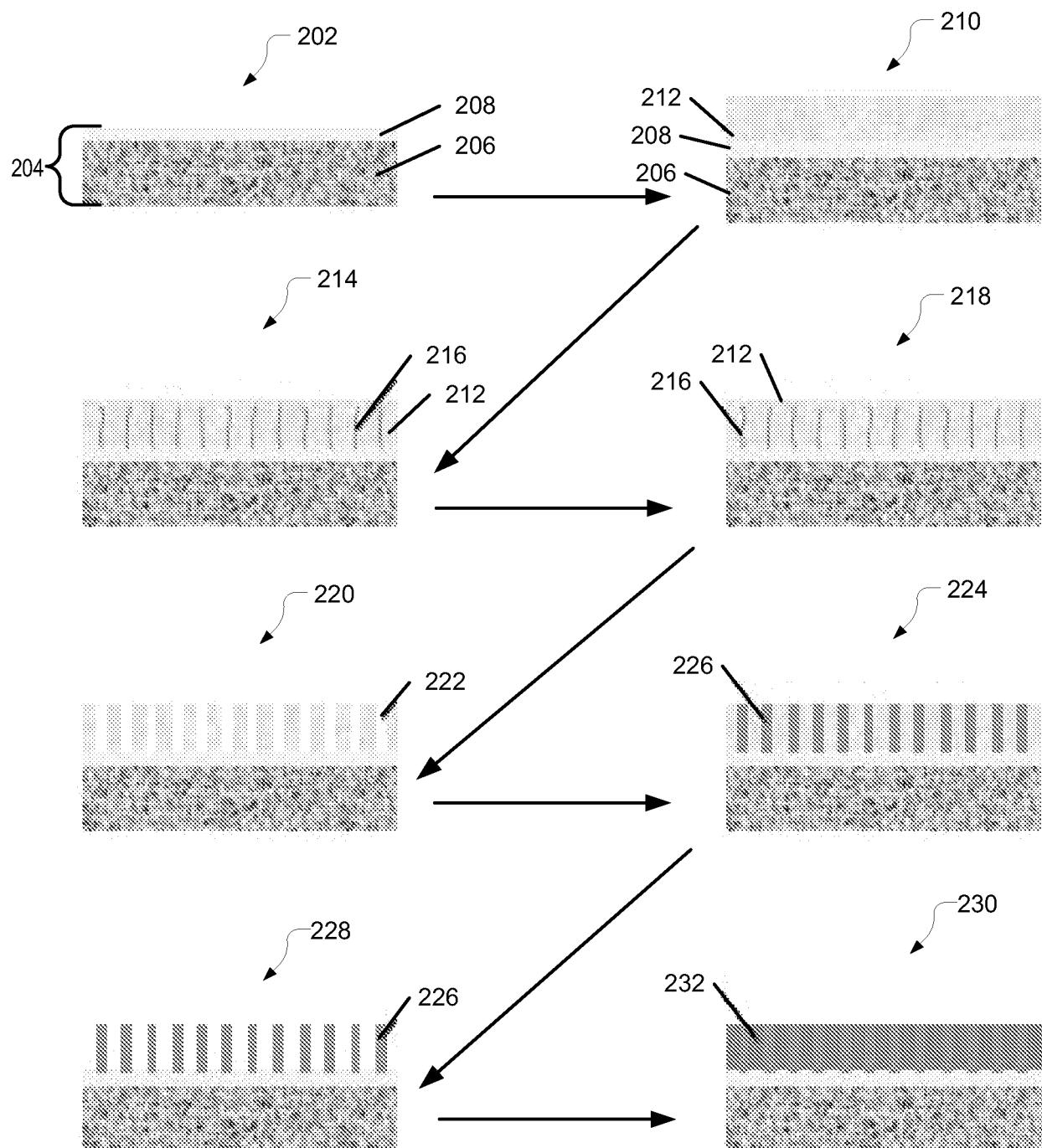
133. The method of claim 119, wherein the HTS layer includes not greater than about 30 vol% nanorods.

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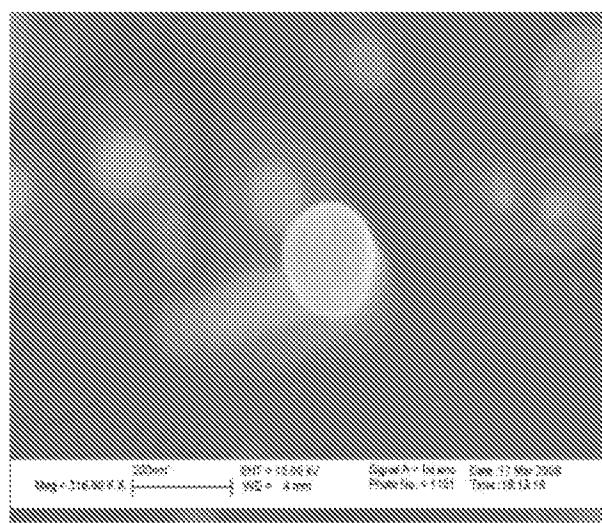
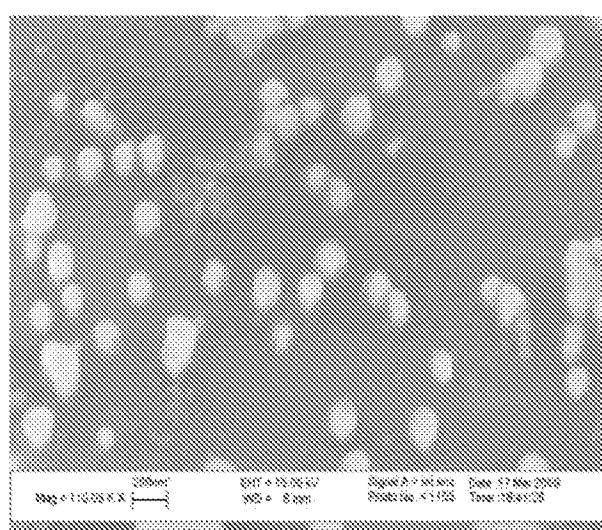
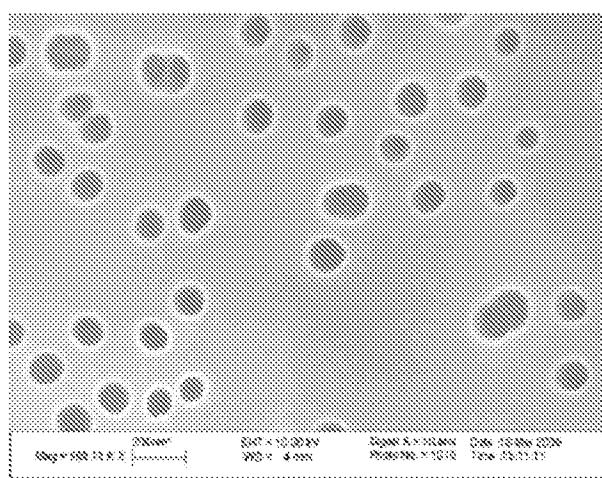


***FIG. 1***

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**FIG. 2**

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***FIG. 3***

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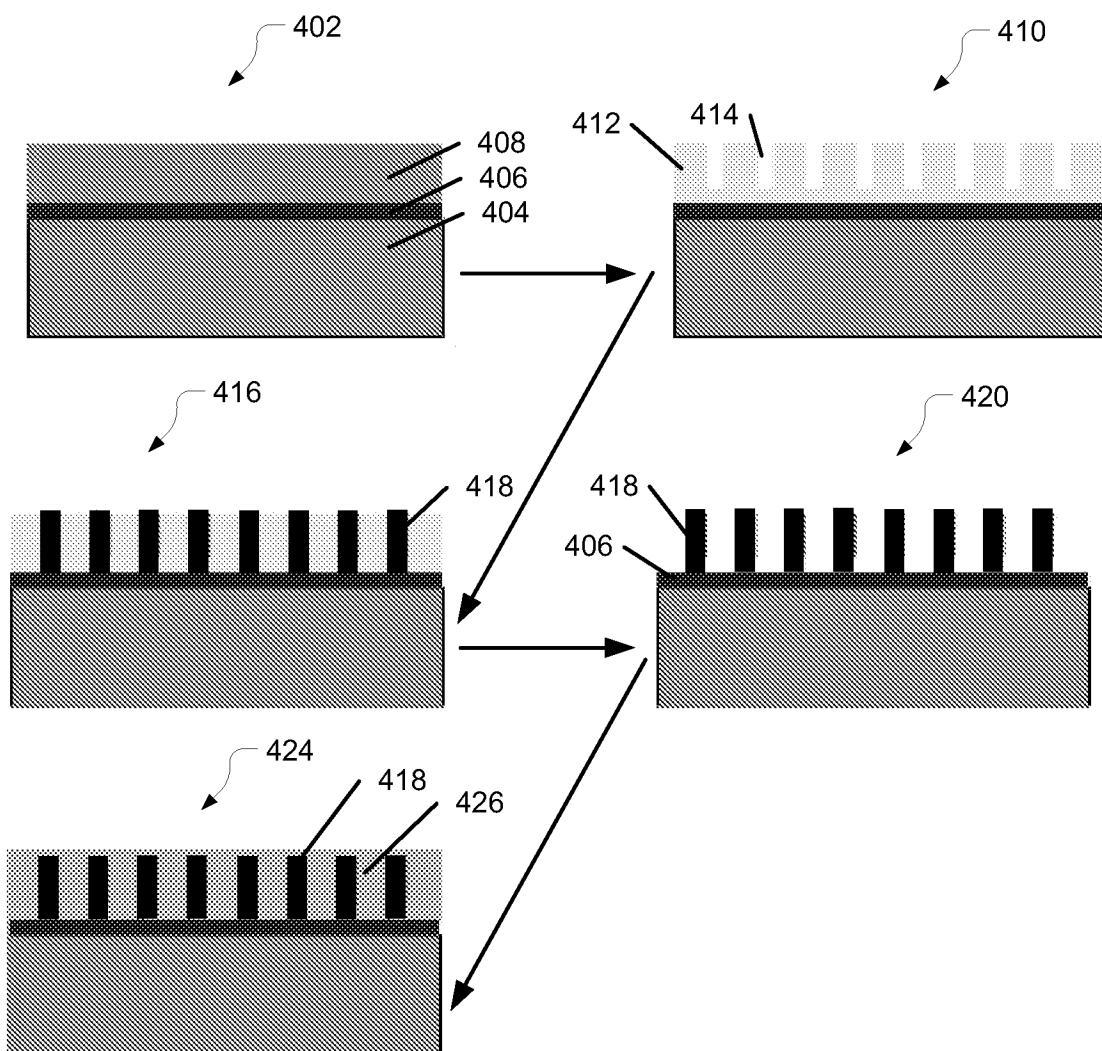
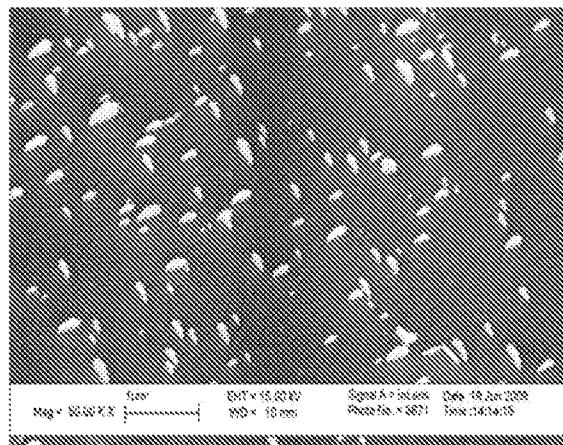
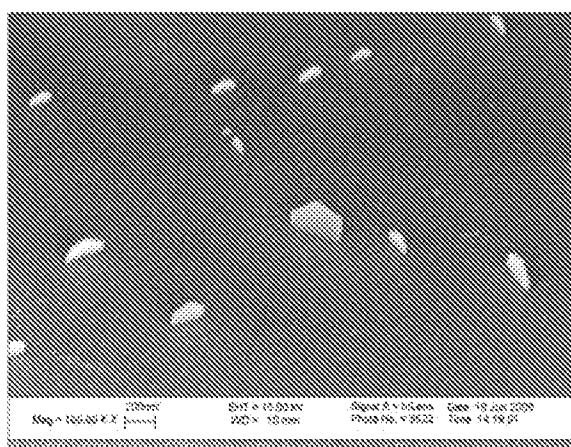


FIG. 4

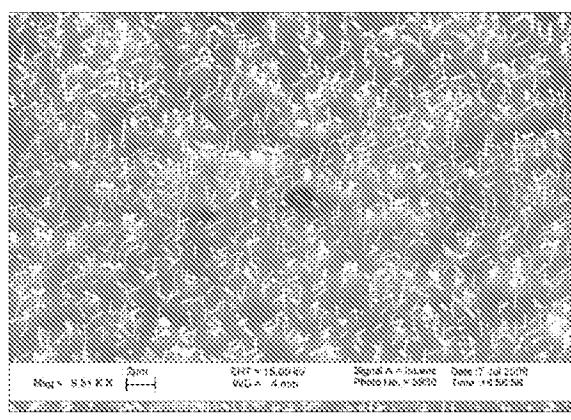
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A



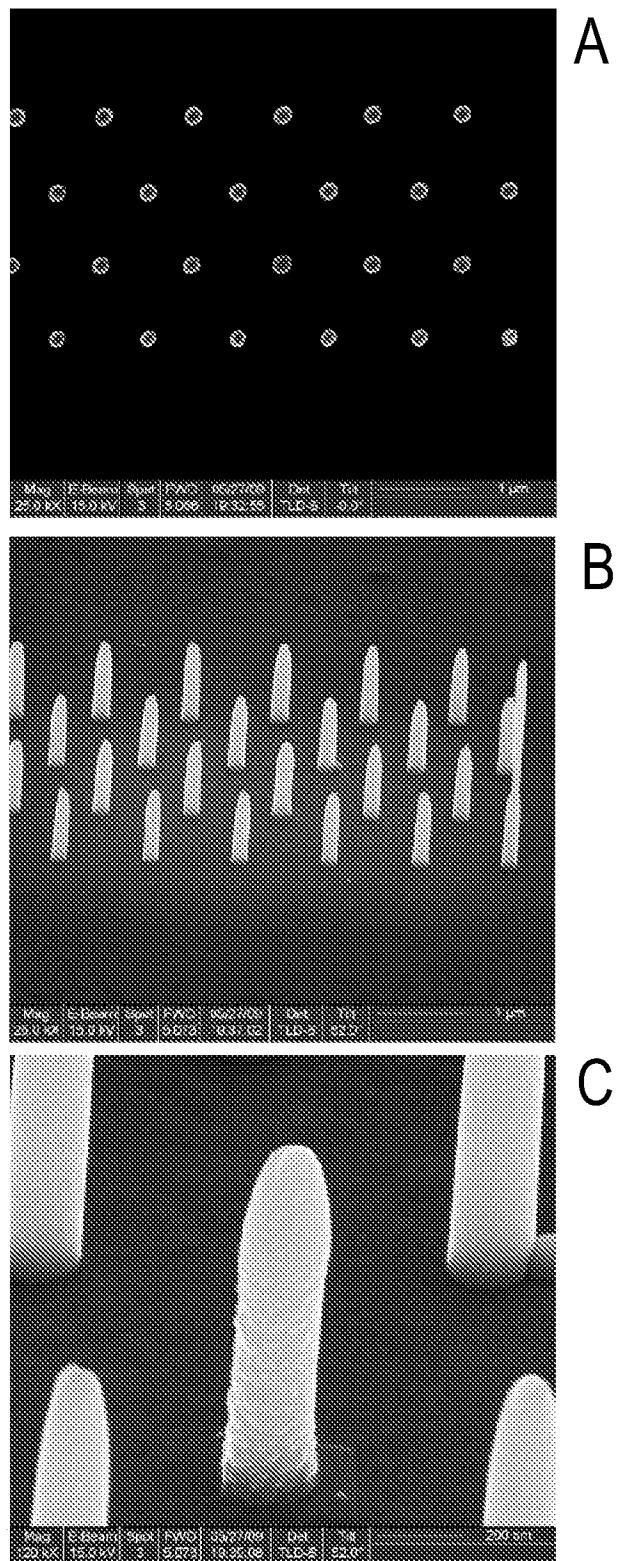
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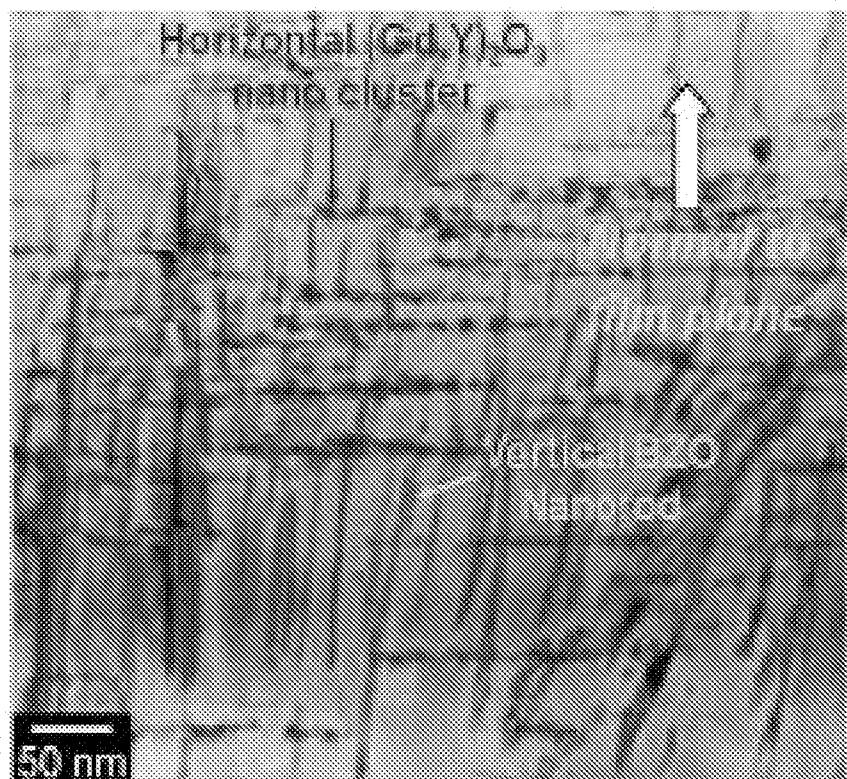
**FIG. 5**

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**FIG. 6**

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**FIG. 7**