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(71) Applicant *(for all designated States except US):* CONDUCTUS, INC. [US/US]; 969 West Maude Ave., Sunnyvale, CA 94086 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : LEE, Luke, P. [US/US]; 395 Ano Nuevo, #1107, Sunnyvale, CA 94086 (US). BURNS, Michael, J. [US/US]; 750 N. Shoreline, #115, Mountain View, CA 94043 (US). CHAR, Kookrin [KR/US]; 704 Chimalus Drive, Palo Alto, CA 94306 (US). LIANG, Guo-Chun [CN/US]; 7634 Squirewood Way, Cupertino, CA 95014 (US). ROWELL, John, M. [US/US]; 102 Exeter Drive, Berkeley Heights, NJ 07922 (US).

(74) Agent: ELCESS, Kimberley; Conductus, Inc., 969 West Maude Ave., Sunnyvale, CA 94086 (US).

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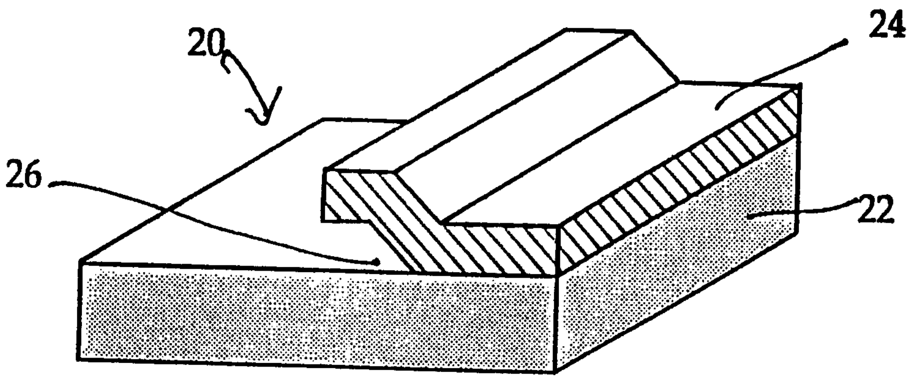

(57) Abstract

A freestanding $YBa_2Cu_3O_{7-\delta}$ or ferroelectric air bridge is disclosed. This structure is useful for membrane detectors and can be extended to applications in which the presence of a substrate can degrade electronic, thermal, and optical properties of the superconductor or ferroelectric structure. The air bridge is fabricated using conventional photolithography, ion-beam dry etching, and selective wet etching. In the preferred embodiment, a sacrificial dielectric layer is deposited between a supportive substrate and a layer of superconducting material. The dielectric layer is later etched away in selected regions to form the air bridge. Step coverage of epitaxial bridge layers has been achieved without significant degradation of the superconducting properties of $YBa_2Cu_3O_{7-\delta}$ layers. Alternatively, $YBa_2Cu_3O_{7-\delta}$ can be used as the sacrificial layer when a ferroelectric such as $Pb(Zr,Ti)O_3$ is the desired air bridge material.

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FREESTANDING STRUCTURES OF PEROVSKITE-TYPE OXIDE MATERIALS

Field of the Invention

This invention relates to freestanding structures incorporating high-quality thin films of perovskite-like oxide materials. In particular, it relates to electronic device structures utilizing unsupported regions of thin films of high-temperature superconductors and ferroelectric materials.

Background of the Invention

Since the discovery by Bednorz and Müller in 1986 of the new class of superconducting oxides, the "cuprates" which have superconducting transition temperatures greater than about 30 K, rapid progress has been made in techniques related to their fabrication. Before this discovery, superconductivity had been observed in many metallic elements as well as in some intermetallic compounds. Metals were well understood as materials, and so the fabrication of useful devices from these superconductors was a fairly straightforward matter.

The new superconductors, however, are ceramics. Where metals are malleable and are easily formed into wires and magnets, ceramics are brittle and fragile, tending to break when stressed. Metals usually melt at reasonable temperatures of a few hundred degrees Celsius, so they can be molded. Ceramics often decompose instead of melting, and must be fired at high temperatures in oxidizing atmospheres. While metals are robust, suffering only local modification when subjected to acids or high energy particles, ceramics may undergo wider ranging damage during chemical attack.

The three major families of high-temperature superconductors are the 1-2-3 compounds such as $YBa_2Cu_3O_{7-\delta}$, the thalium compounds such as TlBaCaCuO (several phases superconduct), and the bismuthates such as BaSrCaCuO (several phases superconduct). In all of these families, the oxide superconductors have a complicated crystal structure based on a simpler structure, that of perovskite $CaTiO_3$, and the superconductors are often said to have a "layered perovskite" structure. This is because in all cases the crystal structure can be thought of as a bottom layer of perovskite, a middle layer, and a top layer of perovskite, where the layers are stacked in the c-direction. No matter how many layers, a c-axis film will always present what appears to be a perovskite unit cell to its substrate and to any layer grown on top of it. Many of the peculiarities of the growth of high-temperature superconductor (HTS) thin films are related to this crystal chemistry.

In the (true) perovskite crystal structure, the O^{2-} and Ca^{2+} ions form a close-packed cubic (face-centered cubic, FCC) structure which then has four octahedral interstices and eight tetrahedral interstices. The O^{2-} anions occupy the cube face centers, the Ca^{2+} cations the cube corners, and the Ti^{4+} cations one-quarter of the octahedral interstices. There are six face centers per unit cell, each shared by two cells, for a total of three "O-sites" per unit cell. Similarly there are eight cube corners per unit cell, each shared by eight cells, for a total of one "A-site" per unit cell. Finally, there are four octahedral interstices per unit cell, but only one is occupied in this structure, so there is one "B-site" per unit cell. Other materials with the simple perovskite structure include $BaTiO_3$, $SrTiO_3$, $SrSnO_3$, $CaZrO_3$, $SrZrO_3$, $KNbO_3$, $NaNbO_3$, $LaAlO_3$, $YAlO_3$, and $KMgF_3$. Many of these minerals are ferroelectric.

"Ferroelectricity" is the spontaneous alignment of electric dipoles by their mutual interaction, and is analogous to ferromagnetism. An applied electric field will align the local electric field in (polarize) a small region of the crystal (called a "domain"), as happens with any non-conducting material. In a ferroelectric, however, if a high enough external field is applied, then when the external field is removed, some polarization of the domains (the remanent polarization) is left. The hysteretic character of the polarization curve leads to applications in non-volatile memory and in piezoelectric transducers. Good perovskite ferroelectrics include $BaTiO_3$, $PbTiO_3$, $NaNbO_3$, $KNbO_3$, $NaTaO_3$, and substituted structures such as $Pb(Zr,Ti)O_3$ (PZT), $Pb_{0.9}La_{0.1}(Zr,Ti)O_3$ (PLZT) and $(Ba,Sr)TiO_3$ in which the A sites are occupied by mixtures of Pb^{2+}, Sr,$^{2+}$, Ba^{2+}, La^{2+}, Ca^{2+}, and Cd^{2+}, and the B sites are occupied by mixtures of Ti^{4+}, Nb^{4+}, Sn^{4+}, Hf^{4+}, Zr^{4+}, Ce^{4+}, Th^{4+}, and Ta^{4+}.

Another common crystal structure for ferroelectric materials is based on the corundum (sapphire, Al_2O_3) structure and is called "ilmenite." The unit cell of corundum has the O^{2-} arranged to form a hexagonal close-packed (HCP) structure, and Al^{3+} ions fill in two-thirds of the octahedral interstices. In ilmenite, $FeTiO_3$, the Fe^{2+} ions fill one-third of the octahedral sites and the Ti^{4+} fill the other one-third of these sites. Alternating layers of cations are either all Fe^{2+} or all Ti^{4+}. Ferroelectrics having the ilmenite structure include $LiNbO_3$ and $LiTaO_3$; in these materials each layer has an ordered arrangement of Li^{2+} and Nb^{4+} or Ta^{4+} ions.

The ilmenite structure is related to the perovskite structure in exactly the same way that the HCP structure is related to the FCC structure. The arrangement of atoms in the close-packed plane of both of these structures is the same, that is, a hexagonal lattice in which each atom has six nearest neighbors. This arrangement has interstices bounded by three atoms, and has two interstitial sites for every atom. In both structures these layers are stacked so that each plane fits tightly into the one below, with each subsequent plane translated so that the atoms match up with one of the interstitial sites in the structure below. In the FCC structure, the layers are stacked A-B-C, that is the atoms in the third layer lie over the interstices in the second layer that match up with interstices in the first layer. HCP stacking is A-B-A, that is the atoms in the third layer lie over the interstices in the second layer that match up with atoms in the first layer. So similar are the perovskite and ilmenite structures, that the two are often lumped together into the same class, called perovskites.

Although the perovskite crystal structure is cubic, most of the perovskite type materials undergo phase transitions between the forming temperature and the use temperature, Tc for the superconductors and the Curie temperature for ferroelectrics. These phase transitions reduce the symmetry of the crystal and allow anisotropic properties to develop. The most useful forms of these materials are generally the orthorhombic structures. In this crystal structure, the angles between all of the major axes are 90° (right angles) but all three axes have slightly different lengths. Similar phase transitions occur in the ilmenite structures.

Bulk specimens, that is, self-supporting pieces, of the high-T_C superconductors contain many separate grains, each a small crystallite having nearly random orientation with respect to its neighbors. This misorientation, along with the properties of the grain boundary itself, lead to reduced current carrying ability in bulk samples. The superconducting properties of bulk samples are often quite different from those of the thin films, making bulk specimens poor choices for the scientific study of the inherent properties of this class of material. Furthermore, preparation of bulk samples is itself rather difficult, and the compromised superconducting properties of this material make it less than ideal for electronic applications.

A similar situation holds for the ferroelectrics. While these materials are not generally used to carry current, their properties, too, depend on crystal orientation and the structural stability problems are the same as for the superconducting perovskites. For applications it is desirable to have the maximum polarization possible. Taking into account the anisotropy of the crystal properties, this maximum polarization is achieved in a single crystal where all of the dipoles are aligned and there are no discontinuities. As with the oxide superconductors, this state is very difficult to achieve. Almost as good, however, is a thin film with a constant and well-defined crystallographic orientation. Such a film has a constant a- or c-axis orientation perpendicular to the plane of the film and has few or no high-angle grain boundaries. Because of the atomic arrangements, grain boundaries of about 0° (±5°) or 90° (±5°) are not too detrimental to the properties of the films. In the art of high-temperature superconductivity these films are referred to as "single crystal" films, although they are not, strictly speaking, a single grain. As a compromise, they will be referred to in this description as "nearly single crystalline" which is defined as having a constant surface normal (vector perpendicular to the plane of the film) and having no high-angle ($5° \leq \Theta \leq 85°$) grain boundaries.

For these and other reasons, the high-T_C oxide, or cuprate, superconductors are most useful when made in thin film form. Films from 5 to 500 nm can be deposited on supportive substrates and processed so that the material becomes superconducting at temperatures as high as 120 K. These films can be patterned into devices and circuits using techniques modified from those used in semiconductor processing. The superconducting devices and circuits that result have far better performance than similar structures made with normal (non-superconducting) metals, and are more convenient to use than are superconducting structures made from older superconductors that require cooling with liquid helium. The necessity of the supportive substrate, however, is a serious drawback for many applications.

Similarly, for electronic applications, thin films of the perovskite and ilmenite ferroelectrics are more appropriate than bulk forms of these materials. For integration into silicon devices and circuits it is desirable to have very little material, so the films must be of the highest possible quality.

Completely unsupported thin films, on the other hand, are extremely fragile. Once the substrate has been entirely removed the film usually falls apart because it lacks cohesiveness across voids or grain boundaries. The fragility is inherent in some cases, while in others it is enhanced by the thinning process. For example, in preparing samples for transmission electron microscopy (TEM) a bulk specimen is cut very thin and then subjected to a combination of ion milling and wet etching, whereas a thin-film sample is sometimes lifted away from its substrate by etching the substrate. Either of these preparation techniques might preferentially attack the superconductor material at defect sites like grain boundaries and voids. A freestanding thin film would be useful for investigating the inherent properties of these materials in the absence of a non-superconducting substrate, but such films are not yet practical to manufacture.

Superconductors have found use as detectors of fields and radiation. In some of these applications, the presence of a supporting substrate is undesirable. For instance, bolometers are infrared radiation detectors. In order to increase their sensitivity to real signals and to reduce their sensitivity to background heat, it is desirable to thermally decouple the bolometer from the substrate. In this way, the bolometer can heat up and cool down much more quickly than its support substrate, and thermal conduction between the substrate and the detector is reduced, reducing the background noise.

For the ferroelectrics, one important application is that of piezoelectric transducers. (Piezoelectricity is the production of an electric field in response to a mechanical stress. Polarized ferroelectrics have very high coupling coefficients, that is, they translate a large fraction of the mechanical force into electric voltage.) With an unsupported thin film of ferroelectric, much smaller mechanical forces could be translated into voltages than when the applied stress is spread to the substrate. This results in much more sensitive pressure sensors and actuators.

The present invention is a superconducting structure which has a high-quality thin film of high-T_c superconductor decoupled from its supportive substrate. To achieve the desirable properties of a high-T_c superconductor thin film, the superconducting layer is deposited on a supportive substrate which is well matched to the superconductor layer. In regions where the superconducting film is to be decoupled from the substrate, however, an intermediate sacrificial layer is deposited. The superconductive layer is deposited over both the substrate and the sacrificial layer and is patterned. Then, the sacrificial layer is removed, leaving the superconductive film only partially supported by the substrate.

Discussion of the Prior Art

Here we describe the fabrication of a freestanding YBCO air bridge that can be used in nanostructures and microcircuit integration. These structures are fabricated with conventional photolithographic processing, ion-beam dry etching, and selective wet etching with an HF solution. This wet etch was first described by W. Eidelloth, W. J. Gallagher, R. P. Robertazzi, R. H. Koch, and B. Oh, *Appl. Phys. Lett. 59*, 1257 (1991). The films described below were grown by laser deposition on either $LaAlO_3$ or yttria-stabilized zirconia (YSZ) substrates, but many deposition techniques and substrate materials can be used. To produce nearly single crystalline films of YBCO and other perovskite-like materials, the films must be grown epitaxially. In epitaxy, a film is deposited on a substrate whose atomic arrangement forms a template for the crystal structure of the film. When a film is grown on a substrate with the same composition, silicon on silicon for example, the process is called homoepitaxy. Since single crystals of the high-temperature superconductors (or perovskite ferroelectrics) are quite rare, YBCO is deposited by heteroepitaxy. More detailed process conditions for epitaxial film growth are described throughout the literature.

Several chemical compositions are known to attack cuprate superconductor materials. Indeed, it has been an area of intense research to discover methods to protect these fragile materials from degradation during routine processing. Even photoresist developer has been observed to damage $YBa_2Cu_3O_{7-\delta}$ thin films. Hydrofluoric acid (HF) shows a very high selectivity, however, attacking some buffer materials at a much higher rate than it attacks $YBa_2Cu_3O_{7-\delta}$.

Materials known to be good substrates or buffer layers for the oxide superconductors are generally also oxides. Sapphire (single crystal Al_2O_3) and lanthanum aluminate (single crystal $LaAlO_3$) are currently the substrates of choice for microwave applications. Although sapphire has a fairly large lattice constant mismatch as well as a thermal expansion coefficient mismatch with $YBa_2Cu_3O_{7-\delta}$, it has the lowest dielectric loss tangent known. Lanthanum aluminate has higher dielectric loss, but is very well lattice-matched to oxide superconductors and films grown on it so far exhibit even lower microwave surface resistance than films grown on sapphire. Other materials which are appropriate for subsequent epitaxial growth of $YBa_2Cu_3O_{7-\delta}$ are $SrTiO_3$, $CaTiO_3$, CeO_2, MgO, and YSZ (yttria-stabilized zirconia or cubic zirconia, $ZrO{:}Y_2O_3$). These materials can be used as substrates and are often used as buffer layers to improve the epitaxy of YBCO, or as dielectrics to insulate two or more superconducting layers. L. P. Lee, K. Char, M. S. Colclough, and G. Zaharchuk, *Appl. Phys. Lett.* *59*, 3051 (1991), discuss the choice of substrate and buffer materials in more detail. Of particular interest in this application, however, is the solubility of several of these buffer and substrate materials in water, HF, or both.

Silicon micromechanical technology is rapidly evolving and a number of innovative fabrication techniques have recently been developed for micromotors and other articulated microstructures. Silicon micromachining is based on depositing and etching structural and sacrificial films. After deposition of the films, the sacrificial material is etched away, leaving a completely assembled micromechanical structure. For the case of polysilicon films, considerable work has been done over the last several years to demonstrate specific applications of such microstructures. Similarly, several techniques for making membranes are known in other art areas. Pressure sensors have been made out of silicon membranes for many years. These achievements have been reviewed in a special section of *Science*, **vol. 254**, Nov. 29, 1991, pp. 1300-1342, and in particular the article by K. D. Wise and K. Najafi on pp. 1335-1342.

The creation of a high-temperature superconductor (HTS) nanostructure technology, or oxide nanostructure technology in general, however, requires techniques and epitaxial multilayer structures which are intrinsically different from conventional Si micromachining technology. This is because HTS microstructures need to be built from an entirely epitaxial technology, in which successive layers must be highly aligned in both the growth direction (out-of-plane orientation) and the plane of the substrate (in-plane orientation). The oxide superconductors are very anisotropic, having an orthorhombic crystal structure, unlike silicon, which is a cubic crystal. This anisotropy, along with their wide range of oxygen contents, make these materials very sensitive to variations in the alignment of individual grains in the films and to crystal defects. We discuss these issues in L. P. Lee, K. Char, M. S. Colclough, and G. Zaharchuk, *Appl. Phys. Lett. 59*, 3051 (1991).

The $YBa_2Cu_3O_{7-\delta}$ (YBCO) air bridge technique described here can be extended to make YBCO membrane structures for detectors and micromachines. See D. B. Rutledge, D. P. Neikirk, and D. P. Kasilingham, "Integrated Circuit Antennas", Chapter 1 in *Infrared and Millimeter Wave*, Vol. 10, (Academic Press, New York, 1983). It can also be applied to micromachining for the fabrication of such nanostructures as micromotors and manipulators.

Objects and Advantages

It is therefore an object of this invention to provide a freestanding thin film of a high-temperature superconductor material, when the film exhibits a high transition temperature (≥ 30 K) and high critical current density ($\geq 10^5$ A/cm^2). To that end we describe a structure in which a thin film of oxide superconductor has been deposited over a patterned dielectric material on a supportive substrate under conditions which result in a high degree of epitaxy and in-plane alignment in the superconductive layer. When the superconductor is patterned, the dielectric material can be removed from selected areas, leaving air bridges: regions where the superconductor film is no longer in contact with the supportive substrate.

It is another object of this invention to provide a freestanding thin film of a ferroelectric material. To that end we describe a structure in which a thin film of oxide ferroelectric has been deposited over a patterned dielectric material on a supportive substrate under conditions which result in a high degree of epitaxy and in-plane alignment in the ferroelectric layer. When the ferroelectric is patterned, the dielectric material can be removed from selected areas, leaving air bridges: regions where the ferroelectric film is no longer in contact with the supportive substrate.

The air bridges impart multiple advantages in performance and operating economy to superconducting and ferroelectric devices. Air bridge bolometers, detectors of infrared radiation, are more sensitive when they are not in contact with a large thermal mass like a supportive substrate which contributes to the background radiation detected by the device. In addition, the reaction time of the sensor is significantly reduced since only the active region needs to detect the radiation and it is not necessary to allow the substrate to come to thermal equilibrium with the detector. Similarly, air bridge switches will have reduced switching times when compared to supported structures. Ferroelectric acoustic sensors and transducers are also more sensitive and quicker to respond when isolated from a supportive substrate.

Thus it is a further object of this invention to provide electronic devices and circuits of high-temperature superconductors which exhibit higher performance than their entirely supported counterparts by virtue of the removal of the supportive substrate in regions of interest. To accomplish this goal, the superconducting properties must not be degraded by the processing sequence, otherwise any advantage gained from the removal of the supportive substrate would be lost.

Another object of this invention, then, is to provide a method for fabricating freestanding structures from thin films of high-temperature superconductor and ferroelectric materials without degrading their electronic properties. The special chemical nature of these classes of compounds, the perovskites and ilmenites, must be taken into account when designing the process. In addition, the process should be manufacturable, that is, it should be robust and reproducible in order to be suitable for volume production.

A further object of the instant invention is to provide a method of micromachining cuprate superconductor materials. The area of nanotechnology is still in its infancy, but the usefulness of miniature motors, pumps, and other mechanical and electromechanical devices is undisputed. The techniques described here are those which must be mastered to make these micromachines from high-temperature superconducting materials. One of the advantages of silicon micromotors is their low power dissipation. A micromotor fabricated entirely from superconducting material needs even less power because it is essentially lossless. Low loss can translate into high speed, broadband operation, and ultra-fine precision.

These and other objects and advantages will become more apparent after consideration of the following detailed description making reference to the drawing figures.

Summary

In brief, then, this invention is directed to a freestanding thin film of high-temperature superconductor material. This structure exhibits all of the desirable properties of a thin film of high-Tc superconductor, including a high transition temperature, a high critical current density, good in-plane alignment, and a lack of high-angle grain boundaries. In addition, the structure contains regions in which the superconducting film is no longer in contact with the supportive substrate. This feature allows the superconductor to be studied without interference from the substrate material. It also allows the active region of a superconductive device or circuit to be thermally and electrically decoupled from the substrate.

Because of the chemical and crystallographic similarities of the perovskite and ilmenite materials, ferroelectric materials and structures can be formed using the same method with only very minor adjustments.

Also disclosed is a manufacturing method for these structures. This process can be used to fabricate not only single structures, but the arrays of devices and circuits described below.

Brief Description of the Drawings

Figure 1 is an artist's rendition of a scanning electron microscope (SEM) microphotograph of the YBCO air bridge.

Figure 2 is a schematic perspective view of a cantilevered beam structure as shown in Figure 1.

Figure 3 is a schematic illustration of the sequence of steps involved in the formation of the YBCO air bridge.

Figure 4 is a schematic perspective view of the bridge structure formed by the steps of Figure 3.

Figure 5 is a schematic perspective view of a cantilevered switch structure with a buffer layer.

Figure 6 is a schematic perspective view of a bridging crossover structure.

Figures 7a and 7b show schematically a bolometer array structure made by the inventive technique. Figure 7a is a side view of part of the structure. Figure 7b is a schematic perspective view of part of the structure.

Figure 8 is a schematic perspective view of an air bridge crossover patterned to allow contact to three individual layers.

Figure 9 is a schematic side view of a membrane formed on a sacrificial substrate.

Figures 10a and 10b show the resistance vs. temperature curves of the YBCO microbridge. Figure 10a shows its R vs. T behavior before the HF wet etch of the $SrTiO_3$ sacrificial layer; Figure 10b shows its R vs. T behavior after the HF wet etch of the $SrTiO_3$ sacrificial layer.

Figures 11a and 11b show the current vs. voltage curves of a YBCO microbridge at 77 K. Figure 11a shows the I-V behavior of the structure before the HF wet etch of the $SrTiO_3$ sacrificial layer; Figure 11b shows the I-V behavior of the structure after the HF wet etch of the $SrTiO_3$ sacrificial layer.

Description of the Preferred Embodiments

A YBCO air bridge **20** fabricated on a $LaAlO_3$ substrate **22** is shown in Figure 1. This cantilevered structure is shown schematically in Figure 2. This 10-µm-wide air bridge **20** was grown over a sacrificial dielectric layer **28** which was subsequently etched away. The bridge **20** is robust enough to stand up to wafer cleaving to leave the freestanding YBCO line seen in the SEM picture.

As illustrated in Figure 3, the following minimum sequence of steps is involved in the formation of YBCO air bridges **20**. Each layer deposited is epitaxial to the remaining underlying layer unless explicitly stated otherwise. Epitaxial deposition results in the "nearly single crystalline" films described above. First, the substrates **22** are cleaned by ultrasonic agitation in acetone and blown dry by clean dry nitrogen gas. Next, epitaxial $SrTiO_3$ **28** is deposited on a $LaAlO_3$ substrate **22** as a sacrificial dielectric layer. After deposition, the $SrTiO_3$ **28** is patterned with conventional photolithographic techniques to form the region of YBCO to be freestanding or suspended. YBCO or another oxide superconductor **24** is then deposited over the patterned dielectric **28**. This superconducting layer **24** is patterned using photolithography followed by dry etching to define the extent of the superconducting regions of the final device structure. Finally, the sacrificial dielectric layer **28** is removed by wet etching to leave a gap **26**. Figure 4 shows a schematic view of this structure. When formed, the gap **26** is instantaneously filled with etchant solution; during operation the gap **26** may be filled with air, a cryogen, or vacuum, but it remains unsupported by the substrate **22**.

In some cases the "substrate" **22** onto which the sacrificial layer **28** is deposited may be a previously grown epitaxial structure **32**, as shown in Figures 5 through 8. This would be desirable, for instance, when the substrate **22** of choice is sapphire. Because sapphire reacts chemically with YBCO and other high-T_c superconductors, a buffer layer **32** must be deposited between the sapphire and any YBCO layer. Thus, in regions where the $SrTiO_3$ **28** will not remain during YBCO deposition a buffer layer **32** must be present. The buffer material may be added before the $SrTiO_3$ has been deposited, or after the $SrTiO_3$ has been patterned. At other times it may be desirable to add an air bridge **20** to a more complicated structure, in which case the substrate **22** may be composed of several layers underneath the sacrificial material **28**. All of these structures fall into the category of "substrate" as used in this disclosure.

The sacrificial dielectric layer **28** can be deposited by any method that will yield an epitaxial layer with the desired crystallographic orientation and surface smoothness. We currently use laser ablation (also known as pulsed laser deposition or PLD), reactive sputtering (on-axis or off-axis), and metal-organic chemical vapor deposition (MOCVD) to deposit dielectric layers. For use as a sacrificial layer **28**, we deposit 300 to 400 nm of an appropriate oxide, *e.g.*, $SrTiO_3$, $CaTiO_3$, or MgO. The particular dielectric material chosen must provide a good template for epitaxial crystal growth of a high-temperature superconductor material and it must be soluble in at least one solvent or solution which attacks the superconductor material much more slowly that it attacks the dielectric material. With these two primary considerations in mind, the choice of a particular material for this layer may be governed by arguments of convenience, expense, or availability.

In our current standard process, we use a positive photoresist, such as AZ® 4620 available from Hoescht Celanese, although negative photoresist could be used as well. The desired pattern is formed in the resist by exposure through an appropriate mask, an optional bake to set the resist, and development of the resist according to the instructions provided by the resist manufacturer. The pattern is transferred to the sacrificial layer by argon ion (Ar^+) milling. The surface of the $SrTiO_3$ **28** regions remaining after this step is 300 to 400 nm above the surrounding bare substrate **22** regions, requiring the subsequently deposited YBCO **24** to traverse a 300 to 400 nm step. In order to provide a high quality epitaxial layer of YBCO 24 across this step, we control the slope of the edge of the $SrTiO_3$ **28** regions by adjusting the angle of incidence of the Ar^+ ion beam. Dry etching techniques are more reproducible than wet chemical etching processes and, in particular, ion beam etching can make smooth and controlled angles for the steps at the edges of the $SrTiO_3$ **28** regions. In this case the incoming ion beam makes an angle of about 45° with the normal to the sample surface. The remaining resist is then stripped with acetone.

For the air bridge **20** itself, we deposit 300 to 500 nm of YBCO. Again, photoresist is used to form a pattern on top of the superconducting layer. We then dry etch this YBCO layer **24** to define the extent of the superconducting regions of the final device. After the patterning is complete, the remaining photoresist is removed.

To convert the $SrTiO_3$-supported air bridge into a freestanding suspended structure, we selectively wet etch the $SrTiO_3$ using a weak HF solution. Previous wet etching tests have indicated that the etching rate for $SrTiO_3$ is approximately 1 μm/min under gentle ultrasonic agitation in a room-temperature solution of 25% HF in water. Similar wet etch tests on thin film layers of YBCO deposited by laser ablation indicated an etching rate of about 4 nm/min. Thus, for properly designed structures, there is no need to passivate the YBCO during this $SrTiO_3$ wet etching process. Although this specific example uses $SrTiO_3$ as the sacrificial dielectric **28**, any appropriate dielectric material could be used with concomitant modifications to the precise processing steps enumerated above.

It is possible to increase the robustness of the air bridge layer **24** by adding a layer of YSZ below and above the superconducting film. A very thin layer is enough to support extremely thin layers of YBCO. To accomplish this, the $SrTiO_3$ is patterned as before, but YSZ is deposited as a buffer layer on top of the patterned layer and substrate. YBCO is then deposited on top of this layer to the desired thickness, and YSZ is deposited on top of the YBCO. Although we specifically recite the use of YSZ it should be understood that this is a mechanical support, so that any high-quality buffer layer material could be used instead of YSZ.

In order to make a freestanding, or partially supported, film of ferroelectric one makes the following substitutions. The substrate **22** is again cleaned, and the sacrificial layer **28** deposited. The same substrate choices are available, but for the sake of illustration, YSZ will be used in this case. Also for illustration, YBCO will be the sacrificial layer **28**. The YBCO is patterned and the ferroelectric, say, PZT, is deposited as bridge layer **24**. This layer **24** is patterned as before into a useful pattern such as a memory device, a transducer, or an electro-optic element. Again, the sacrificial YBCO layer **28** is removed leaving a gap **26**, but here the etchant is chosen to have a much higher rate of dissolution of YBCO **28** than of ferroelectric **24**. Most acids attack YBCO much faster than they attack other oxides. For example, in this case diluted HNO_3 will remove the YBCO while leaving all of the other materials in the structure. A good dilution ratio is 0.5% HNO_3 (off the shelf, that is, prediluted) in H_2O. Other acids, such as HCl, can be substituted as long as they etch YBCO much faster than the other materials.

For cases in which it is desirable to use a non-superconducting non-ferroelectric material in these structures, $PrBa_2Cu_3O_{7-\delta}$ is completely interchangeable with $YBa_2Cu_3O_{7-\delta}$.

A variation of this process, shown in Figure 9, is to use a substrate **22** of sacrificial material. In this case, the substrate **22** is cleaned and a buffer layer **32** (if desired) is deposited, followed by superconductor **24**. The back side of the substrate **36** is then patterned and etched away in selected regions to form a membrane of superconductor **24**.

The superconducting properties of the YBCO were examined to identify any possible degradation from the above processing steps. For the electronic transport measurements, the samples were mounted on a temperature-controlled copper sample platform which was inserted into a liquid helium dewar above the liquid helium level. Although the temperature of the copper sample platform was controlled by a commercial temperature controller to within 10 mK, the samples were open to the colder helium gas. Thus, if the thermal conductance of the suspended air bridges is sufficiently low, the center portion of the air bridges should be below the temperature of the copper sample holder and the sample substrate. In Figure 10a we show the resistance versus temperature curve for an air bridge before the sacrificial $SrTiO_3$ was removed. For this sample, the YBCO air bridge was ~300 nm thick, 10 µm wide and after the removal of the $SrTiO_3$ sacrificial layer the suspended portion was 50 µm long. The figure shows a transition at 87 K with a width of about 1 K. In Figure 10b we show the resistance versus temperature for the same sample as in Figure 10a after removal of the $SrTiO_3$ sacrificial layer. As can be seen from a comparison of Figures 10a and 10b, there was no appreciable degradation in the width of the superconducting transition by the $SrTiO_3$ removal process. As can also be seen by comparison of Figures 10a and 10b, the air bridge, once suspended, was cooled by the helium gas to about 3 degrees below the temperature of the substrate. Thus its superconducting transition occurred when the copper sample platform and substrate were at 90 K. Since these photolithographically defined YBCO air bridges can be thermally decoupled from the underlying substrate, it should be possible to create monolithic YBCO bolometer arrays on a single substrate using standard photolithography techniques.

In Figures 11a and 11b we show I-V curves for the air bridge whose R vs. T behavior is shown in Figures 10a and 10b. The data was taken with the copper sample platform held at 77 K. The critical current of the air bridge before it was suspended was 5 milliamps at 77 K (Figure 11a). This corresponds to a critical current density of $\sim 1.3 \times 10^5$ amps/cm^2. This reduced current density may indicate that "step edge" junctions formed at the edges of the $SrTiO_3$ sacrificial layer. See K. P. Daly, W. D. Dozier, J. F. Burch, S. B. Coons, R. Hu, C. E. Platt, and R. W. Simon, *Appl. Phys. Lett. 58*, 543 (1991) for a discussion. After the $SrTiO_3$ etch process to suspend the air bridge, the critical current was 3 milliamps while the sample platform was held at 77 K (Figure 11b). The $SrTiO_3$ etch which produced this sample was 2 minutes long to accommodate the etching of some larger structures on the same chip set. Although the etch rate of the YBCO is considerably slower than the etch rate for $SrTiO_3$ (0.004 µm/min versus 1 µm/min), the YBCO was reduced ~0.008 µm in width. Since both the top and the underside of the air bridge are exposed to the HF solution, the YBCO was reduced 8 to 16 nm in thickness. Thus its cross-sectional area was reduced from 4 µm^2 to ~3.8 µm^2. This reduction in cross-sectional area should have caused a reduction in critical current of ~0.25 milliamps, from 5 milliamps to ~4.75 milliamps. An examination of the air bridges using SEM (Figure 1) did not show any obvious cracks or constrictions. The fact that the observed reduction in critical current was a factor of 8 larger (~2 milliamps) might indicate that the region which produced the before-etch depressed critical current was more sensitive to the etching process than the rest of the YBCO. For example, it would not be unreasonable for the YBCO etch rate to be enhanced somewhat at the edges of the $SrTiO_3$ layer due to the large localized stresses. Nevertheless, the data in Figures 10a, 10b, 11a, and 11b indicate that freestanding YBCO structures can be fabricated without a large degree of degradation in the intrinsic superconducting properties.

Exemplary Applications

The fabrication sequence disclosed herein is useful for producing several superconductive structures. Below we discuss several specific exemplary applications of this technology.

Switches and Insulating Crossovers

Figures 5 and 6 show air bridges used as crossovers. In Figure 5 the bridging superconducting or ferroelectric layer **24** contacts the support structure **22, 32** at only one edge while the other edge is suspended. This produces a cantilevered structure which may be useful as a switch or sensor. In Figure 6 the bridging superconducting or ferroelectric layer **24** contacts the support structure **22, 32** at both edges producing a true bridge.

Both of these structures are useful as sensors and switches. Under normal conditions, the bridging superconductor layer **24** is electrically isolated from supported superconductor layer **34**. No current flows between the two layers and the switch is "open." When an external force is applied to bridging superconductor layer **24** it deflects toward supported superconductor layer **34**, eventually approaching close enough to "close" the switch and allow current to flow from one layer to the other. Physical contact is not necessary since the electrons are able to tunnel across a very small air (or other non-superconducting) gap. A ferroelectric sensor operates much the same way, except that depression of the cantilever does not cause a current to flow, rather a voltage is developed.

The force can be induced in a number of ways. If the lever or bridge **24** is depressed physically, the switch acts as a pressure sensor. A magnetic field will repel the superconducting lever or bridge **24** so that the switch will be sensitive to magnetic fields. For some applications, the magnetic field can be induced by a control line carrying electrical current in proximity to the switch.

Air is a very good insulator. In these air bridge configurations, the air gap **26** can take the place of a traditional dielectric or insulating material.

Bolometers

Figures 7a and 7b show an array structure **30** suitable for bolometer arrays. This type of structure has many advantages for bolometer construction. Unlike typical bolometer fabrication techniques, this bolometer structure is monolithic. There is no need to thin an auxiliary structure and later attach it. Thus the technology of this invention is more convenient for manufacturing. In addition, the freestanding structures have very low thermal capacity and very low thermal mass. The low thermal capacity, due to the very small volume that reacts to the incoming infrared signal, makes the bolometer more sensitive. The low thermal mass, since it is not coupled thermally to a large substrate, reduces the background signal significantly. Finally, the ease of assembling several bolometers into an array makes imaging feasible. This array of detectors yields spatial as well as chemical information.

Microwave Switches

Another application that follows from the low thermal resistance of the air bridge structure is a microwave switch. For microwave use, the switching time of a component must be very fast. A very fast switch results when an air bridge **20** is thinned laterally to reduce its cross-sectional area between two regions of broader superconductor. To switch from the normally closed to the open state of the switch, the air bridge material is forced to go normal, that is, to transform from the superconducting state to the non-superconducting state. This is accomplished by exceeding either the critical current, the critical magnetic field, or the critical temperature of the material in the air bridge. Due to the slower response time of the surrounding areas and to their greater cross-sectional area, only the air bridge undergoes this change of state.

Micromotors

A micromotor can be made using the above techniques to pattern a dielectric layer in addition to the superconductor layers. When the dielectric piece is allowed to move freely between two charged plates of a capacitor, it can be made to rotate by applying a changing voltage to the plates. The motor can then be used as a sensor or an actuator, since any change in the dielectric's local environment will change the rotation speed or direction, and the motion of the motor itself can be used to move other parts of a circuit. For example, this motion can be used to change the width of a gap between two parts of another capacitor in the system in order to change the capacitance and resonant frequency of the circuit. The motion can also be used to produce (or detect) ultrasonic or acoustic waves in the motor's vicinity.

Economy

One practical advantage of air bridges is the reduction in physical and thermal mass that results from the elimination of dielectric layers. Because superconductors must be cooled to superconduct, thermal mass reduction is desirable. Smaller, lighter structures require less coolant than larger, heavier ones. This translates into less expensive cooling technology and extended time between coolant replenishing. In addition, many of the air bridge devices have particular utility in satellites and spacecraft where size and weight reductions are most welcome.

Conclusion, Ramifications and Scope

It is thus apparent that we have successfully fabricated superconducting air bridges thus demonstrating a suspended HTS microstructure capable of being exploited for device applications. Although many of the mechanical properties of HTS oxides films are not known, we have shown a general approach to making suspended HTS structures analogous with that found in silicon microcircuit technology. This opens the possibility for numerous HTS applications in sensors and micromachines.

We have also disclosed several devices made with air bridges. These devices incorporate high-temperature superconductors and encompass sensors, actuators, imaging arrays, and microwave components.

While the above description contains many specific details, these should not be construed as limitations on the scope of the invention, but rather as an exemplification of one of its preferred embodiments. Many other variations are possible and will no doubt occur to others upon reading and understanding the preceding description. Accordingly, the scope of the invention should be determined not by the embodiment illustrated, but by the appended claims and their legal equivalents.

Claims

What is claimed is:

1. A multilayer ceramic structure, comprising:
   a supportive crystalline substrate,
   a bridge layer of nearly single crystalline ceramic material comprising at least two regions,
   wherein the first region of said bridge layer is in contact with and is epitaxial to said supportive crystalline substrate,
   and the second region of said bridge layer is separated from said supportive crystalline substrate by a gap.
2. The structure of claim 1 wherein said nearly single crystalline ceramic material is a superconductor at all temperatures below about 30 K.
3. The structure of claim 1 wherein said nearly single crystalline ceramic material is a ferroelectric.
4. The structure of claim 1 wherein said second region of said bridge layer further comprises a parallel region and a rotated region, said parallel region having an in-plane orientation whose major axes are parallel to the major axes of said supportive crystalline substrate, and said rotated region having an in-plane orientation whose major axes are rotated with respect to the major axes of said supportive crystalline substrate.
5. The structure of claim 1 wherein said supportive crystalline substrate comprises a planar substrate and a buffer layer epitaxial to said planar substrate.
6. The structure of any of claims 1–5 wherein said supportive crystalline substrate further comprises a supported layer of nearly single crystalline ceramic material,
   wherein said supported layer is epitaxial to said buffer layer and is entirely supported by said buffer layer.
7. The structure of any of claims 1–6 wherein said nearly single crystalline ceramic material has a crystal structure of the perovskite or ilmenite type.
8. A method of forming a structure on a supportive crystalline substrate, comprising the steps of:
   depositing a sacrificial layer epitaxially on said supportive crystalline substrate,
   forming said sacrificial layer into a desired pattern, said pattern comprising a first region and a second region, said sacrificial layer being selectively removed from said first region and said sacrificial layer remaining in said second region,
   depositing a ceramic layer, said ceramic layer being epitaxial to said supportive crystalline substrate in said first region and said ceramic layer being epitaxial to said sacrificial layer in said second region,
   and selectively removing the remainder of said sacrificial layer.
9. The method of claim 8 further comprising the steps of forming said ceramic layer into a desired pattern.

10. An electronic device structure, comprising:
a supportive crystalline substrate,
a bridge layer of nearly single crystalline ceramic material comprising at least two regions,
wherein the first region of said bridge layer is in contact with and is epitaxial to said supportive crystalline substrate,
and the second region of said bridge layer is separated from said supportive crystalline substrate by a gap,
and wherein an electronic device is formed in said bridge layer.

11. The device of claim 10 wherein said bridge layer is sensitive to infrared radiation.

12. The device of claim 10 wherein said bridge layer is sensitive to an external magnetic field.

13. The device of claim 10 wherein said bridge layer is sensitive to a pressure differential.

14. The device of any of claims 10–13 wherein said nearly single crystalline ceramic material is an oxide superconductor.

15. The device of any of claims 10–13 wherein said nearly single crystalline ceramic material is a ferroelectric.

16. The device of any of claims 10–15 wherein said nearly single crystalline ceramic material has a crystal structure of the perovskite or ilmenite type.

17. The device of any of claims 10–14, further comprising an intermediate layer of superconducting material,
wherein said intermediate layer of superconducting material is epitaxial to said supportive crystalline substrate
and wherein said first region of said bridge layer is in contact with said intermediate layer of superconducting material , and said second region of said bridge layer is separated from said intermediate layer of superconducting material by a gap.

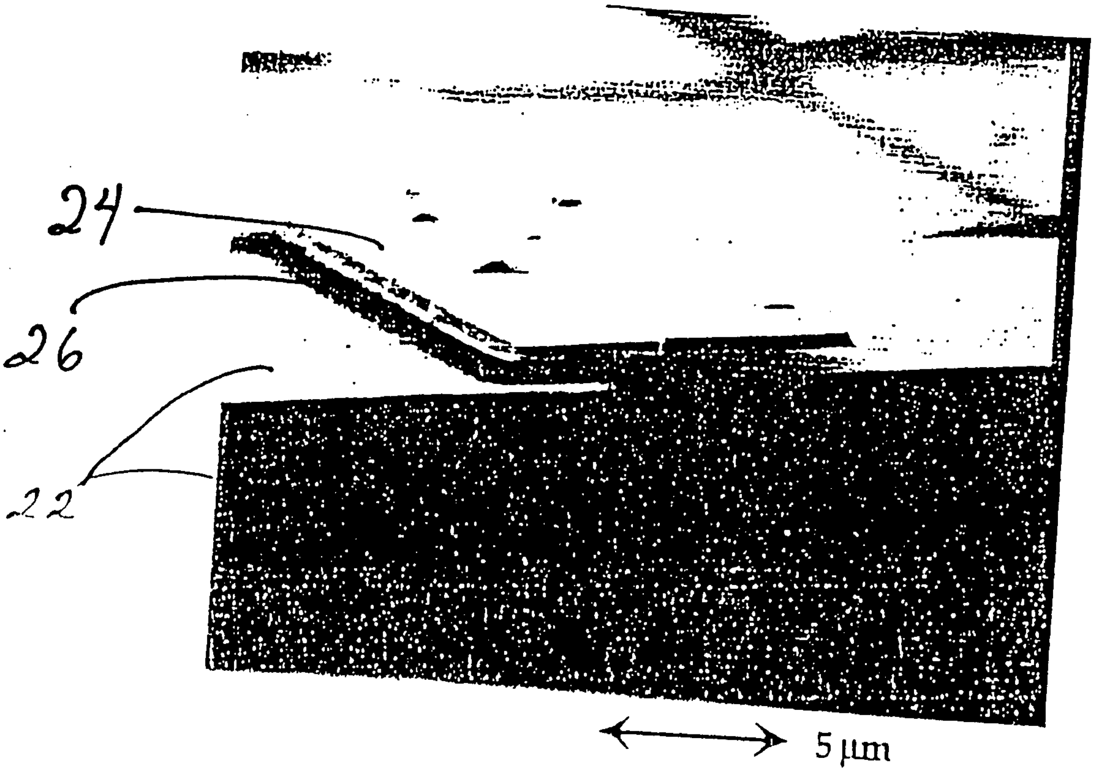


Figure 1

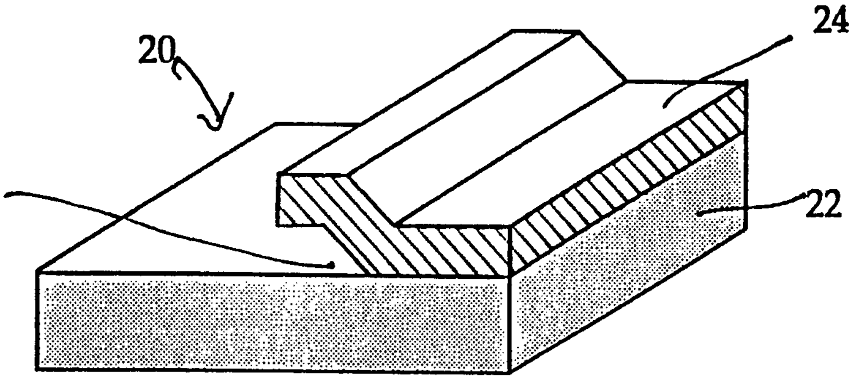


Fig. 2

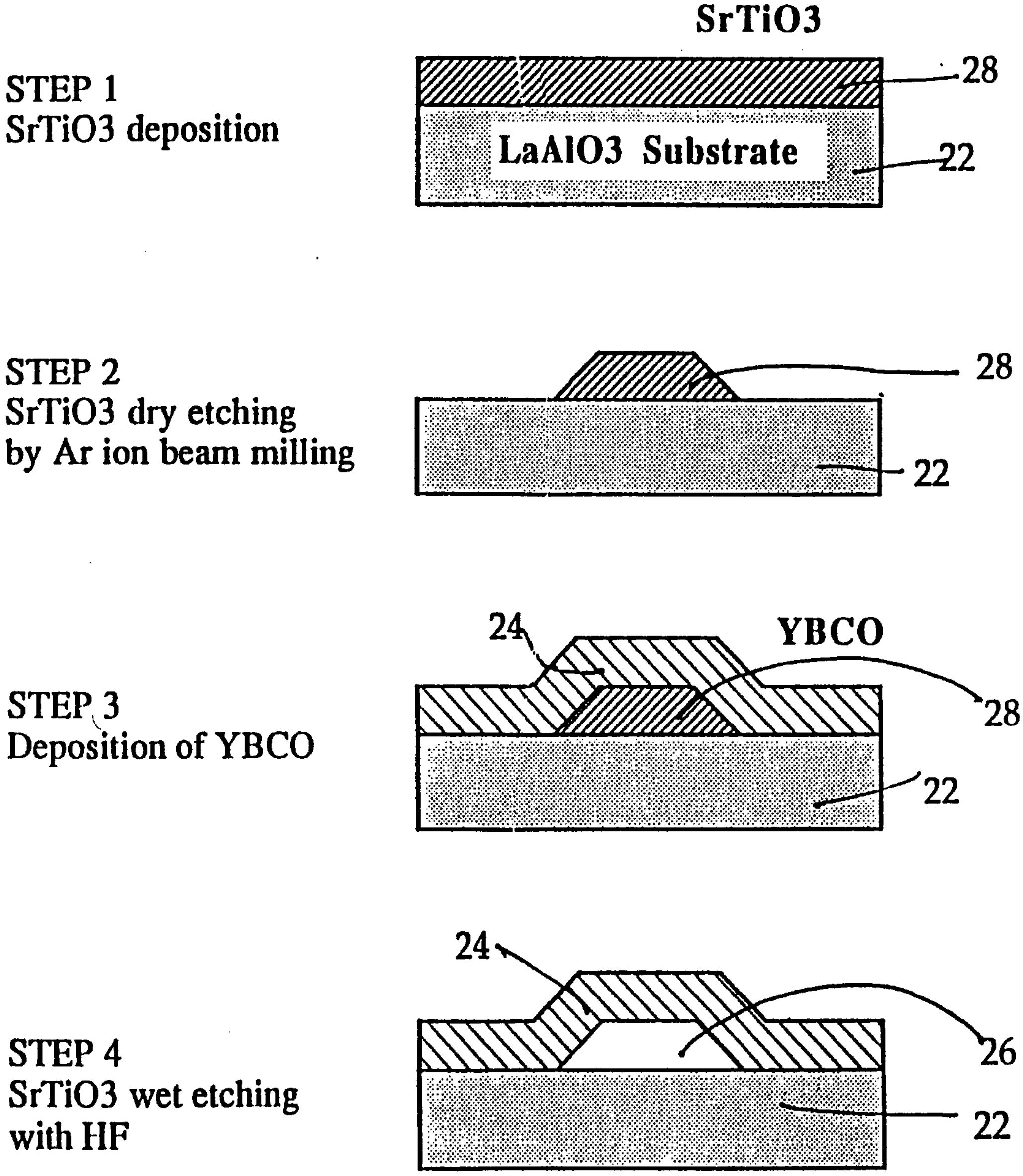

SrTiO3
STEP 1
SrTiO3 deposition
28
LaAlO3 Substrate
22
STEP 2
SrTiO3 dry etching
by Ar ion beam milling
28
22
24
YBCO
STEP 3
Deposition of YBCO
28
22
24
STEP 4
SrTiO3 wet etching
with HF
26
22

Fig. 3

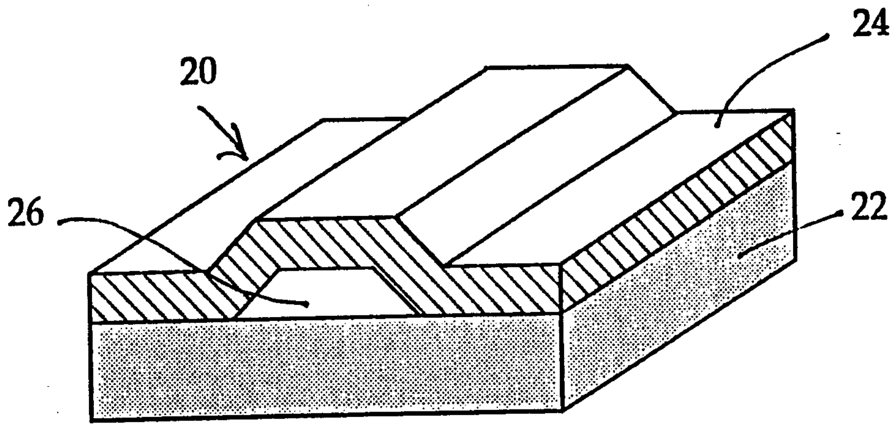


Fig. 4

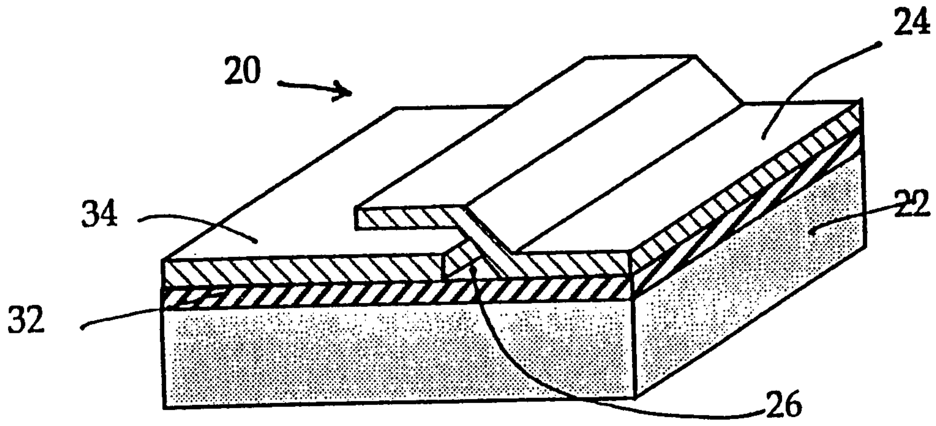


Fig. 5

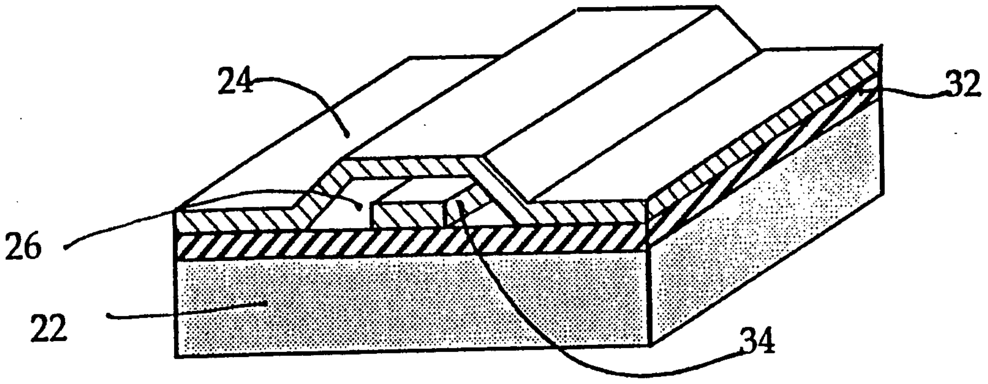


Fig. 6

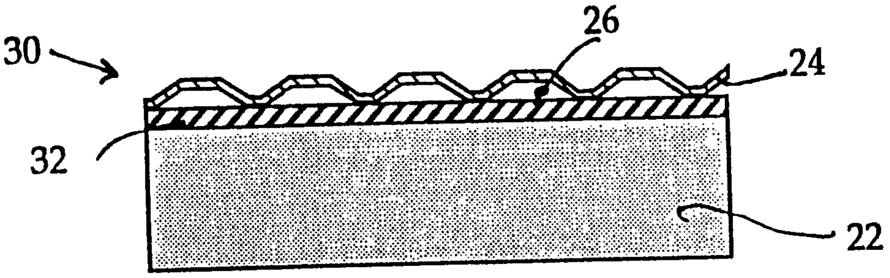


Fig. 7a

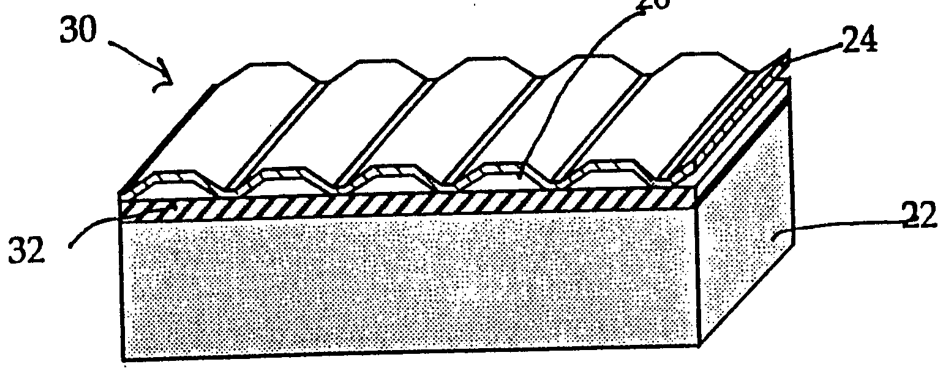


Fig. 7b

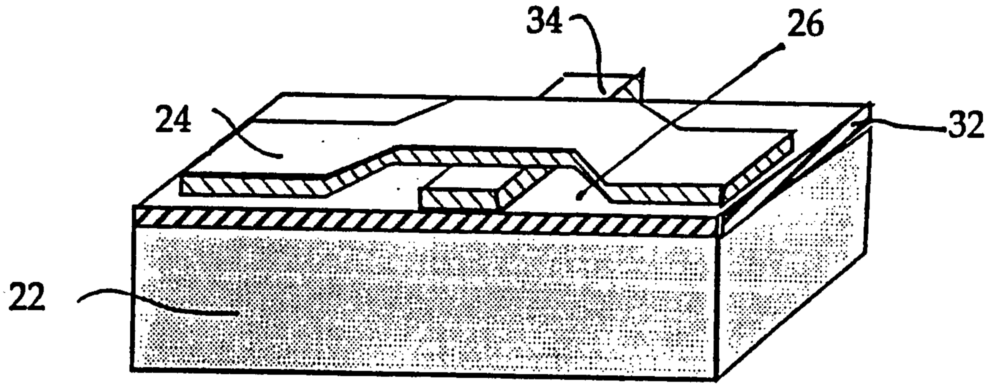


Fig. 8

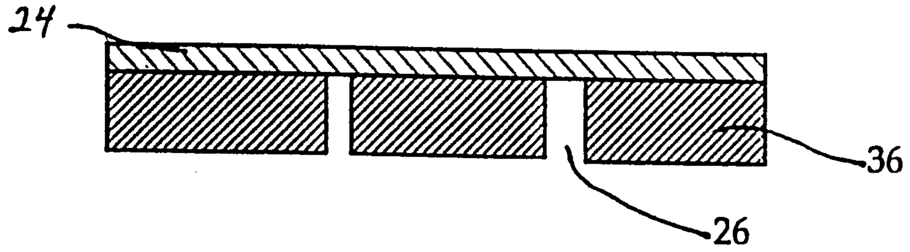
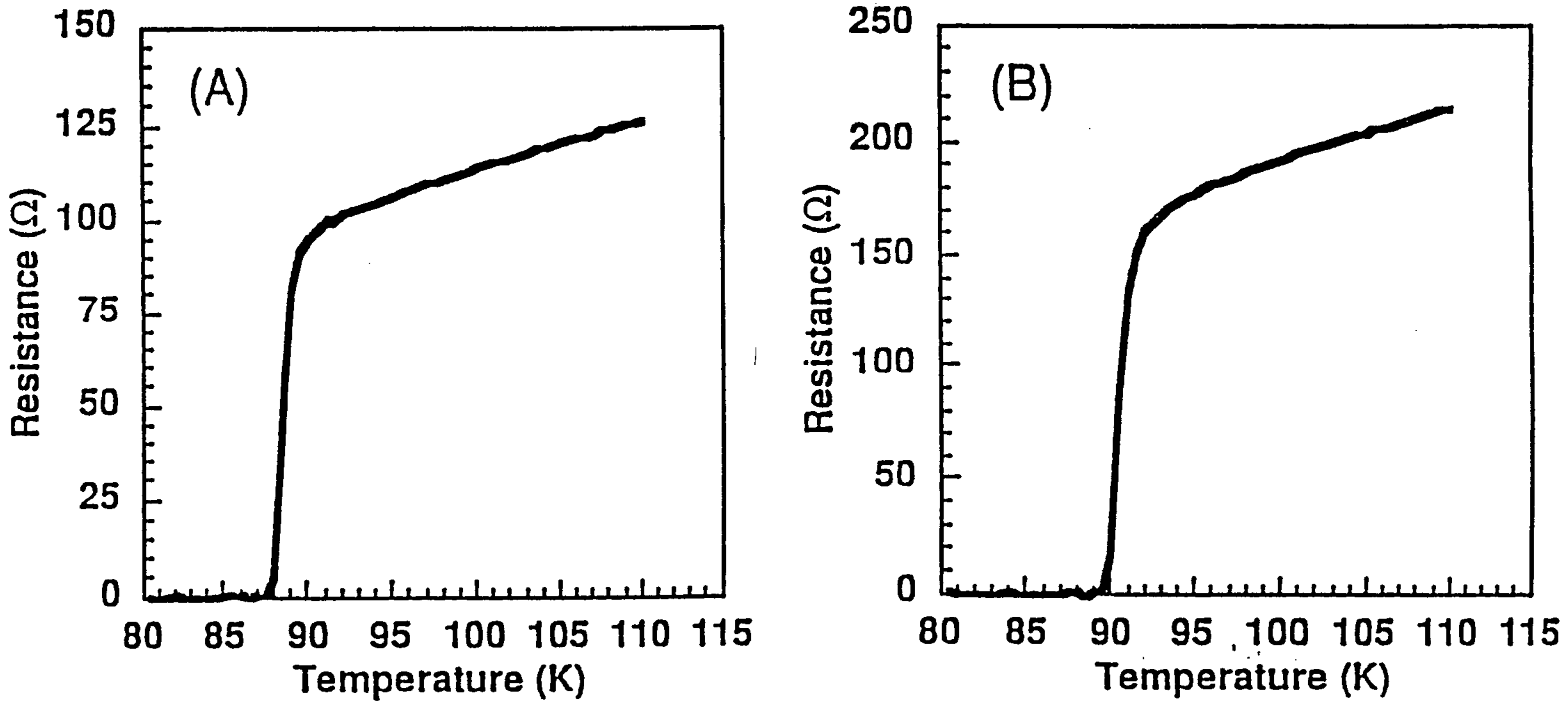


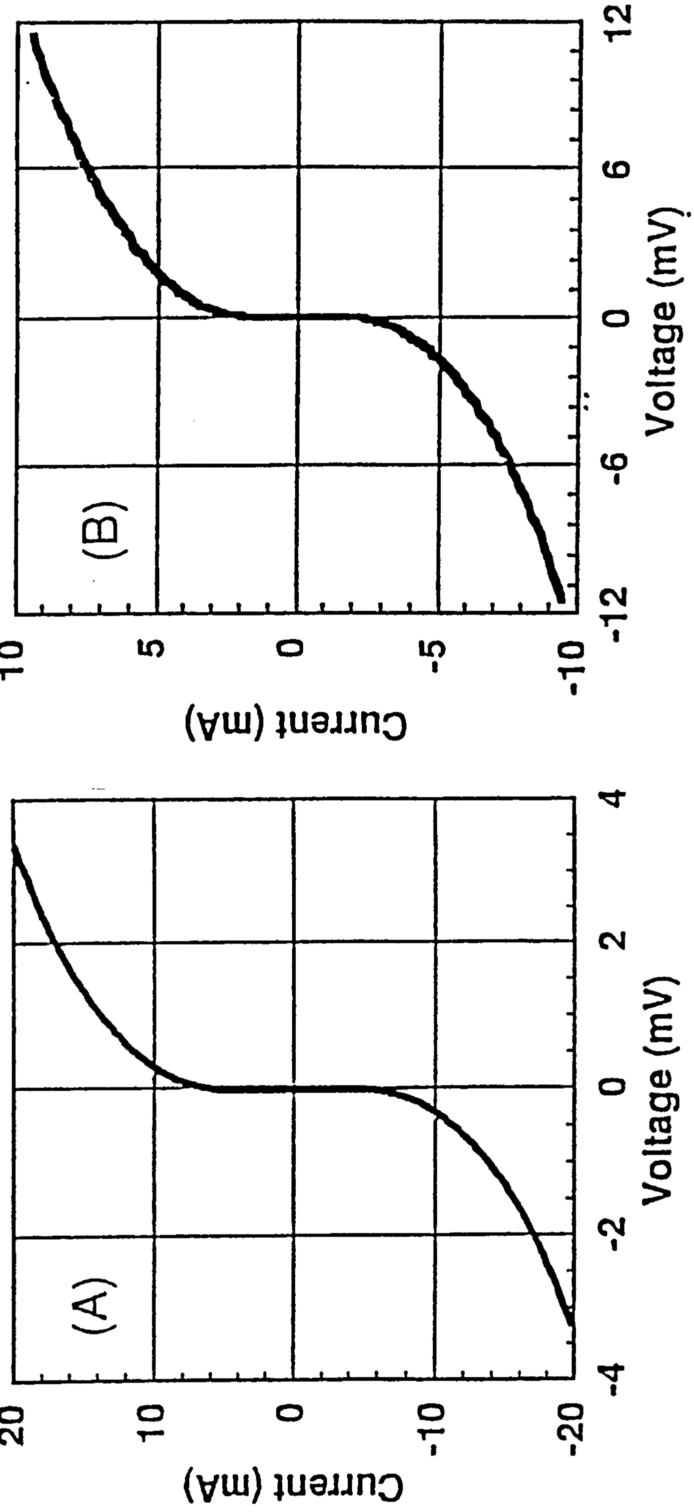
Fig. 9


(A)
Resistance (Ω)
150
125
100
75
50
25
0
80
85
90
95
100
105
110
115
Temperature (K)
(B)
Resistance (Ω)
250
200
150
100
50
0
80
85
90
95
100
105
110
115
Temperature (K)

(a)

(b)

Figure 10


(a)
(A)
Current (mA)
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10
0
-10
-20
Voltage (mV)
-4
-2
0
2
4
(b)
(B)
Current (mA)
10
5
0
-5
-10
Voltage (mV)
-12
-6
0
6
12

Figure 11