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PATENT APPLICATION
Navy Case No. 76,340

SUPERCONDUCTOR AND NOBLE METAL COMPOSITE FILMS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a composite material film (and/or thin film) and a method of preparation wherein the composite material has a low critical current density and a high critical temperature. The invention particularly relates to a composite of a superconductor such as $YBa_2Cu_3O_{7-\delta}$ (YBCO) or $Bi_2Sr_2Ca_2Cu_3O_x$ or $Bi_2Sr_2Ca_1Cu_2O_x$ (BSCCO) and one or more noble metals such as gold and/or silver upon a substrate, each material deposited at a desired thickness upon a substrate wherein magnetic vortices in the superconductor are easily moved.

Description of the Related Art

There is considerable interest in superconducting flux flow and fluxonic devices. *See* Hohenwater et al., *Characteristics of superconducting flux-flow transistors,* IEEE Trans. Magn., vol. 27, pp. 3297-3300 (March 1991), incorporated herein by reference in its entirety and for all purposes. *See also* Kadin, *Duality and fluxonics in superconducting devices,* J. Appl. Phys., vol. 68, pp. 5741-5749 (December 1990), incorporated herein by reference in its entirety and for all purposes. These devices are based on the motion of either Abrikosov or Josephson vortices and require a material whose material properties do not impede the flow of magnetic flux. The high pinning strengths of $YBa_2Cu_3O_{7-\delta}$ (YBCO) have made it unsuitable for flux flow devices without modifying the YBCO in some manner such as thinning or taking advantage of naturally occurring defects such as the grain boundary junction formed over a substrate step. *See* Martens et al., *S-parameter measurements on single superconducting thin-film three-terminal devices made of high T_c and low T_c materials,* J. Appl. Phys., vol. 65, pp. 4057-4060 (May 1989), incorporated herein by reference in its entirety and for all purposes. *See also* Martens et al., *Flux flow microelectronics,* IEEE Trans. Appl. Super., vol. 3, pp. 2295-2302 (March 1993), incorporated herein by reference in its entirety and for all purposes.

Researchers have sought practical, three terminal, superconducting devices for applications in hybrid technologies and on-chip integration with passive, superconducting components. Such devices included the flux-flow transistor and the fluxonic junction transistor, both of which require a superconducting material in which vortices can easily move.

High quality high temperature superconductor (HTS) thin films having "easily movable vortices" are difficult to fabricate. High quality thin films of YBCO generally have T_c's approaching 90 K (degrees Kelvin) and J_c's at 77 K greater than 1×10^6 A/cm^2 and show strong vortex pinning. In such materials, vortex motion is difficult except very close to T_c or in very high magnetic fields (10's of Tesla). *See* Rose-Innes et al., *Introduction to Superconductivity, 2nd Edition*, International Series in Solid State Physics, Vol. 6, Pergamon Press, New York, at pp. 186-190 (1978), incorporated herein by reference in its entirety and for all purposes.

Materials having low vortex pinning (easy vortex motion) usually have a reduced T_c and J_c and are chemically unstable in the ambient environment. This is because the material within or at the grain boundaries often consists of impurities or off-stoichiometric material causing a reduced T_c, J_c and chemical stability, respectively. For example, oxygen-deficient YBCO films which have reduced T_c's and J_c's as well as weak pinning have been shown to be very susceptible to damage from device processing and exposure to water-based chemicals. *See* L. H. Allen et al., *Thin film composites of Au and* $YBa_2Cu_2O_{7-\delta}$, Appl. Phys. Lett., vol. 66(8), pp. 1003-1005 (20 February 1995), incorporated herein by reference in its entirety and for all purposes. Once these materials are fabricated into vortex flow devices, they degrade and change their operating characteristics with age.

Even materials that were initially high quality are susceptible to processing damage. For example, weak-link microbridges fabricated from high-quality materials have exhibited "enhanced" vortex motion. However, when made and used in flux flow devices, they are often operated at reduced temperatures because the T_c of the microbridge is degraded by the patterning process. *See* Miyahara et al., *Vortex Flow Characteristics of High-*T_c *Flux Flow Transistors*, J. Appl. Phys., vol 75, pp. 404 (1994), incorporated herein by reference in its entirety and for all purposes. Furthermore, the stability with time of these devices is uncertain because of the inherent chemical instability associated with degraded superconducting material.

Summary of the Invention

It is therefore an object of the present invention to provide a composite material that consists of a random array of Josephson junctions in which Josephson vortices can easily move throughout the composite material film.

It is therefore another object of the present invention to provide a composite material that consists of a random array of Josephson junctions in which Josephson vortices can easily move throughout the composite material film and the composite material will exhibit variably controlled J_c without a marked decrease in the T_c of the superconductor and be chemically stable.

It is therefore another object of the present invention to provide a composite material that consists of a random array of Josephson junctions in which Josephson vortices can easily move throughout the composite material wherein the material "as-grown" will have the desired property of easy flux motion and avoid extra steps for device processing.

It is therefore another object of the present invention to provide a process for making a composite material that consists of a random array of Josephson junctions in which Josephson vortices can easily move throughout the composite material.

It is therefore another object of the present invention to provide a composite material that consists of a random array of Josephson junctions in which Josephson vortices can easily move throughout the composite material (e.g. film) wherein the composite material can be incorporated into a fluxonic junction diode.

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It is therefore another object of the present invention to provide a composite material that consists of a random array of Josephson junctions in which Josephson vortices can easily move throughout the composite material (e.g. film) wherein the composite material can be incorporated into a bolometric device.

These and other objects are accomplished by making a composite material according to the process (I) of:

(a) providing a substrate;

(b) forming a noble metal layer having a first thickness upon said substrate; and

(c) depositing a superconductor layer having a second thickness at a temperature wherein said metal layer forms puddles exposing regions of substrate and said superconductor deposits between said puddles on said exposed regions of said substrate.

Alternatively, these and other objects may also be accomplished by making a composite material according to the process (II) of:

(a) providing a substrate;

(b) forming a noble metal layer having a first thickness upon said substrate;

(c) heating said noble metal layer to a sufficient temperature to form puddles of noble metal exposing underlying regions of substrate; and

(d) depositing a superconductor layer having a second thickness on said exposed regions of said substrate.

The composite material formed by the above process comprises:

(a) a substrate layer having puddles of noble metal deposited on said substrate wherein said puddles of said noble metal layer have a first thickness; and

(b) said substrate layer having a superconductor layer deposited on said substrate between said puddles deposited on said substrate wherein said superconductor layer has a second thickness.

Brief Description of the Drawings

A more complete appreciation of the present invention and several of the accompanying advantages thereof will be readily obtained by reference to the following detailed description when considered in conjunction with the accompanying drawings, wherein:

FIG. 1 is a schematic of a cross-sectional view of an exemplary composite material made according to the present invention wherein silver paste (silver paste not shown) is used to hold substrate 10 on the substrate holder (holder not shown) and the noble metal puddles of exemplary silver 20 and exemplary superconductor YBCO 30 are deposited on substrate 10. The exemplary silver regions denoted as 20 have an exemplary first thickness of about 3250 Å and exemplary YBCO regions denoted as 30 have an exemplary second thickness of about 800 Å. Also, MgO is the exemplary substrate region denoted as 10. Note the scale of 6 microns associated with FIG. 1. The exemplary composite material of FIG. 1 is made according to Example 3 and referred to as OA493, *infra*. The area denoted as 40 is merely a reflection of an edge of the substrate 10.

FIG. 2 is a schematic top view of another exemplary composite material made according to the present invention. Regions marked as 20 represent a noble metal (e.g. silver is the exemplary metal used in FIG. 2) and regions marked as 30 represent a superconductor (e.g. YBCO is the exemplary superconductor used in FIG. 2). The exemplary silver regions denoted as 20 have an exemplary first thickness of about 2000 Å and exemplary YBCO regions denoted as 30 have an exemplary second thickness of about 850 Å. Though not shown, the exemplary substrate 10 is MgO. Note the scale of 25 microns associated with FIG. 2. The exemplary composite material of FIG. 2 is made according to Example 1 and referred to as OA449, *infra*.

FIG. 3(a) depicts a cross-sectional schematic of substrate 10 coated with a layer of a noble metal 20 (e.g. silver, gold or mixtures thereof). The formation of a layer of noble metal 20 upon substrate 10 is accomplished according to step (b) of the presently claimed process (I). (*See* **Summary of the Invention**, *supra*).

FIG. 3(b) depicts a cross-sectional schematic of substrate 10 coated with puddles of noble metal 20, the puddles 20 having a first thickness. The puddles of FIG. 3(b) being formed from the layer of the noble metal depicted in FIG. 3(a). The formation of a layer of noble metal 20 upon substrate 10 is accomplished according to step (b) of the presently claimed process (I). (*See* **Summary of the Invention**, *supra*).

FIG. 3(c) depicts a cross sectional schematic of substrate 10 with puddles of noble metal 20, and regions of a superconductor 30 deposited on regions of substrate 10 not occupied by puddles of noble metal 20. The exemplary superconductor YBCO refers to regions 30. The deposition of a superconductor is accomplished according to step (c) of the presently claimed process (I). (*See* **Summary of the Invention**, *supra*).

FIG. 4 is a plot of J_c, the critical current density (expressed in Amps/cm^2 units) versus the thickness (the thickness measured prior to forming the puddles i.e. the thickness of the noble metal layer as depicted in FIG. 3(a)) of exemplary silver puddles (expressed in Å units) of an exemplary composite material of about 800 Å of YBCO and various thickness of exemplary Ag. Note that J_c is reduced with increasing Ag thickness. The substrate is MgO.

FIG. 5 is a plot of current, I (expressed in mA units), versus voltage (expressed in μV units) for an exemplary composite material with 840 Å thick Ag and 800 Å thick YBCO regions at a temperature of 78 Kelvin, the plots being made from data taken in the presence of an externally applied magnetic field of varying strengths (e.g. no external field applied, 50 Gauss external field applied, 125 Gauss external field applied, 250 Gauss external applied field). The substrate upon which the Ag and YBCO is deposited is MgO. Note that small, applied fields cause significant reductions in J_c and an increase in sample voltage at a given current.

FIG. 6 is a plot of resistance, R (expressed in Ω units), versus temperature (expressed in degrees Kelvin) for each of several exemplary composite materials with exemplary Au being deposited at varying first thicknesses and YBCO deposited at a second thickness of about 2000 Å upon a MgO substrate. Note that while the superconducting onset temperature remains high, the T_c is lowered with increasing thickness of Au.

FIG. 7 is a plot of voltage change (expressed in μV units) versus current (expressed in mA units) for the Au/YBCO composite of FIG. 6 wherein the voltage variation is measured due to a 3 Gauss applied external magnetic field at selected temperatures (expressed in degrees Kelvin).

FIG. 8 contains two plots: (1) of temperature (expressed in degrees Kelvin) versus resistance (expressed in Ω units) and (2) of temperature (expressed in degrees Kelvin) versus photoresponse (expressed in μV units) of a Au/YBCO thin film bridge wherein the bias current is as indicated (the bias current being expressed in mA units) and wherein the composite thin film comprised of about 2000 Å thickness of YBCO and about 500 Å thickness of Au. The results were obtained using a He-Ne 2mW laser as the light source.

Description of the Preferred Embodiments

The following detailed description of the invention is provided to aid those skilled in the art in practicing the present invention. However, the following detailed description of the invention should not be construed to unduly limit the present invention.

Variations and modifications in the embodiments discussed may be made by those of ordinary skill in the art without departing from the scope of the present inventive discovery.

Please note that throughout this patent application a reference to the thickness of the noble metal puddles means the thickness of the noble metal layer when the noble metal layer is a continuous layer as exemplarily depicted in FIG. 3(a). The thickness of the puddles refers to the thickness of the noble metal layer prior to the noble metal coalescing into puddles or islands of noble metal as exemplarily depicted in FIGS. 3(b) and 3(c), respectively. Thus, the thickness of the noble metal is as indicated by the angstroms of thickness assigned to the noble metal layer as stated herein (*infra* **and *supra***). Typically, the thickness of the noble metal after the noble metal forms puddles **(i.e. thickness of puddles as in FIGS. 3(b) and 3(c))**, has an average thickness near the thickness of the contiguous (unpuddled) noble metal layer **(i.e. thickness of noble metal as in FIG. 3(a))**.

With respect to superconducting materials, the T_c is the critical temperature of a material below which temperature the superconducting material exhibits no measurable resistance to current flow. In addition, a superconducting material also has a J_c which is the critical current density. If a current is passed through a sample of superconducting material and if the current is above I_c, the critical current, then the superconducting sample exhibits a measurable resistance. The value of J_c is proportional to the value of I_c ($J_c = I_c$ / cross-sectional area of current flow). The lower the value of J_c, the lower the value of I_c and, therefore, the lower the threshold current that is required to move (i.e. unpin) vortices.

The purpose of this invention is the fabrication of thin film high temperature superconductors (HTS) with the important material property of "easily moved" magnetic vortices. This property can usually be associated with material having a low critical current density resulting from reduced intergranular coupling. Exemplary composite material films of exemplary YBCO and a noble metal such as Ag or Au (or mixtures thereof) exhibit this property. The superconducting onset temperature is not significantly reduced in these composite material films, suggesting that the exemplary YBCO grains are of high quality and that the gold or silver form a clean interface with the exemplary YBCO. The noble metal in these composites segregates from the YBCO and moves into the grain boundaries, producing a two dimensional array of Josephson junctions (i.e. superconductor region--normal metal region--superconductor region: see FIGS. 1, 2, 3(c)). The Josephson junction is an SNS or SIS junction wherein S is a superconductor, N is a normal metal and I is an insulator. These composite material films are candidate materials for fabricating three terminal HTS devices which rely on vortex interactions for the control of electron transport. These composite material films also have potential applications in non-linear superconducting devices, bolometers, and non-bolometric photodetectors.

The composite material film (or thin film) of a superconductor and one or more noble metals (e.g. Ag, Au or mixtures thereof) described herein are fabricated by the deposition of the superconductor onto a thin film of the noble metal(s). Noble metal exemplary thicknesses up to about 5000 Å were used in the development of these composite materials. If the noble metal is Ag, a thickness (of the noble metal layer puddles; see FIGS. 3(a-c), *infra*)) of up to about 5 times the thickness of the superconductor may be used. If the noble metal is Ag, a thickness (of the noble metal layer puddles; see FIGS. 3(a-c), *infra*) of down to about 1/10 the thickness of the superconductor may be used. The thickness of the superconductor layer can exemplarily be varied from about 500 to 5000 Å. Typically, for the exemplary Ag metal, the thickness of the puddles is between about 200 to about 4,500 Å. More typically, for the exemplary Ag metal, the thickness of the puddles is between about 300 to about 4000 Å. Most typically, for the exemplary Ag metal, the thickness of the puddles is between about 400 to about 3500 Å. Preferably, for the exemplary Ag metal, the thickness of the puddles is between about 500 to about 3000 Å. More preferably, for the exemplary Ag metal, the thickness of the puddles is between about 600 to about 2,500 Å. Most preferably, for the exemplary Ag metal, the thickness of the puddles is between about 800 to about 2000 Å. If the noble metal is Au, a thickness (of the noble metal layer puddles; see FIGS. 3(a-c), *infra*)) of up to about 1 times the thickness of the superconductor may be used. If the noble metal is Au, a thickness (of the noble metal layer puddles; see FIGS. 3(a-c), *infra*) of down to about 1/10 the thickness of the superconductor may be used. Typically, for the exemplary Au metal, the thickness of the puddles is between about 200 to about 2000 Å. More typically, for the exemplary Au metal, the thickness of the puddles is between about 250 to about 1750 Å. Most typically, for the exemplary Au metal, the thickness of the puddles is between about 300 to about 1500 Å. Preferably, for the exemplary Au metal, the thickness of the puddles is between about 350 to about 1000 Å. More preferably, for the exemplary Au metal, the thickness of the puddles is between about 375 to about 750 Å. Most preferably, for the exemplary Au metal, the thickness of the puddles is between about 400 to about 600 Å.

The noble metal is deposited onto a substrate at, for example, room temperature by any method onto a substrate which is compatible with the superconductor also to be deposited onto the substrate. The exemplary noble metals may be Ag or Au or mixtures thereof. The exemplary purity of the noble metals used was about 99.9%; however, any purity sufficient to produce composites with high T_c's and low J_c's and sufficient chemical stability may be used. Exemplary methods for depositing noble metal(s) onto the substrate include sputtering, evaporation, laser ablation, chemical vapor deposition. Sputtering may be conventional or off-axis sputtering or inverted cylindrical magnetron (ICM) sputtering (e.g. for YBCO deposition). Evaporation may be thermal evaporation or electron beam evaporation. Chemical vapor deposition may be metal organic chemical vapor deposition (MOCVD). Also, the noble metal(s) and superconductor may be deposited by any deposition process upon the substrate which does not require a post deposition anneal to temperatures above the melting point of the noble metal. Other methods of depositing the noble metal(s) (i.e. one or more noble metals) are well known in the art. Deposition of the noble metal is typically carried out at ambient temperatures or chemical vapor deposition temperatures wherein the substrate is stable at the noble metal deposition temperatures.

After deposition of a thin film of one or more noble metals upon a substrate, a superconducting material is deposited onto the noble metal layer at a temperature sufficient to coalesce the contiguous noble metal layer (depicted as 20 in FIG.3(a)) into puddles (depicted as 20 in FIGS. 3(b) and 3(c), respectively) exposing the underlying substrate (depicted as 10 in FIG. 3(b)) and causing the deposition of a superconductor onto the exposed regions of the substrate 10 between the noble metal layer puddles 20 (see FIG. 3(b)) to form a composite as depicted in FIG. 3(c). Note that there are no regions of the upper substrate surface that remain exposed after deposition of both the noble metal and superconductor. Typical superconductors include YBCO and BSCCO, among others. Any of the yttrium based superconductors, bismuth based superconductors and thallium based superconductors may be used in conjunction with the present invention. Additionally, any high temperature superconductor compatible with Ag or Ag may be used in place of exemplary YBCO.

For the deposition of a superconductor onto a substrate with an Ag noble metal layer, the deposition is generally carried out at a temperature range, typically, between about 600 to about 800 °C, more typically, between about 625 to about 775 °C, most typically, between about 650 to about 770 °C, preferably, between about 655 to about 765 °C, more preferably, between about 660 to about 760 °C, and most preferably, between about 670 to about 750 °C. However, the temperature range for the deposition of the superconductor may be any temperature suitable or sufficient for the growth of the superconductor onto the surface of the substrate and sufficiently high to cause the metal layer to form puddles without being so high as to destroy the composite film of substrate, superconductor and noble metal.

For the deposition of a superconductor onto a substrate with an Au noble metal layer, the deposition is generally carried out at a temperature range, typically, between about 725 to about 850 °C, more typically, between about 750 to about 825 °C, most typically, between about 775 to about 815 °C, preferably, between about 785 to about 805 °C, more preferably, between about 790 to about 803 °C, and most preferably, between about 795 to about 800 °C. However, the temperature range for the deposition of the superconductor may be any temperature suitable or sufficient for the growth of the superconductor onto the surface of the substrate and sufficiently high to cause the metal layer to form puddles without being so high as to destroy the composite film of substrate, superconductor and noble metal.

Methods for the deposition of the superconductor include sputtering, evaporation, laser ablation, chemical vapor deposition. Sputtering may be conventional or off-axis sputtering or inverted cylindrical magnetron (ICM) sputtering. Evaporation may be thermal evaporation or electron beam evaporation. Chemical vapor deposition may be metal organic chemical vapor deposition (MOCVD). Other methods of depositing the superconductor are well known in the art. Any *in situ* deposition technique is acceptable for the fabrication of the superconductor component of these composite material films.

Deposition of the superconductor is carried out at temperatures noted above or at chemical vapor deposition temperatures wherein the substrate, the noble metal and the superconductor is stable (e.g. chemically stable, thermally stable etc.) at superconductor deposition temperatures.

A variety of substrates may be used in conjunction with the present invention. Exemplary substrates include MgO, $SrTiO_3$ (STO), $LaAlO_3$ (LAO) and yttria stabilized zirconia (YSZ). However, any substrate that is compatible with growth of a superconductors such as YBCO, BSCCO, yttrium based superconductor, bismuth based superconductor, and thallium based superconductor, respectively, and is compatible with Au and/or Ag deposition may be used.

Gold and silver are not very reactive metals. Therefore, these noble metals (e.g. Ag and/or Au) do not adhere very well to many substrates. The increased surface mobility at high temperatures (e.g. temperatures at which superconductors such as YBCO are grown) allows these metals to coalesce into small puddles on the substrate and form a discontinuous film. This migration of the noble metal together with the deposition of the superconductor (e.g. YBCO) results in a composite material film of superconductor/noble metal (e.g. YBCO/Ag or YBCO/Au). The morphology of the composite material film (e.g. YBCO/Au) is such that the noble metal forms islands (i.e. puddles) surrounded by a superconductor (e.g. YBCO) or vice versa (i.e. YBCO islands or puddles surrounded by noble metal) depending upon the thickness of the noble metal and/or the thickness of the superconductor, the substrate used, and deposition conditions.

Additionally, the noble metal also forms along the superconductor grain boundaries (e.g. YBCO grain boundaries) creating arrays of SNS Josephson junctions. FIGS. 1 and 2 illustrate the morphology of an exemplary YBCO/Ag composite material film fabricated from 850 Å of YBCO onto 2000 Å of silver upon an exemplary MgO substrate. The exemplary silver forms islands (i.e. puddles 20) on the exemplary MgO substrate 10 surrounded by a background of exemplary well-connected YBCO grains 30.

The electrical properties of these composite material films are strongly dependent on the substrate 10 used and the relative amounts of noble metal (n.b. amount of noble metal used is proportional to the thickness of the noble metal layer formed) and amounts of superconductor (n.b. amount of superconductor used is proportional to the thickness of the superconductor layer formed). For example, for some of the Ag composites, T_c is essentially independent of Ag thickness below approximately 3500 Å and rapidly decreases with increasing amounts of silver. At 3750 Å of Ag, the superconducting transition is incomplete. J_c is relatively constant for silver thicknesses below about 2500 Å and rapidly decreases with further increase in Ag thickness. For example, for a composite material film with 800 Å of YBCO, the effect of Ag thickness on J_c is illustrated in FIG. 4. J_c was measured at a reduced temperature $\mathbf{t = T/T_c = 0.46}$. The value of T_c for the various composite material films plotted in FIG. 4 is about 80 degrees Kelvin. The effects of an external magnetic field on J_c of these composite material films is of considerable importance in device applications. The presence of the noble metal within the grain boundaries allows intergranular Josephson currents to be controlled by external magnetic fields. Exemplary high quality YBCO films require applied fields of 10's of Tesla to affect J_c's, but practical device operation is limited to several Gauss. The reduction in critical current for applied magnetic fields of 0 Gauss, 50 Gauss, 125 Gauss and 250 Gauss, respectively, applied to an exemplary YBCO/Ag composite material film (e.g. 800 Å YBCO and 840 Å Ag) is shown in the I-V traces of FIG. 5. The external applied magnetic field was applied perpendicular to the composite material film sample which consisted of a bar of the composite material film approximately 2 mm wide and 1 mm long, held at a temperature of about 78 degrees Kelvin. The J_c reduction by applied fields on the order of about 50 to about 250 Gauss indicate that these composite material films are useful for HTS devices that are based on "easily moved" magnetic vortices.

The morphology and electrical characteristics of the exemplary YBCO/Au composite material films are similar to those of the exemplary Ag composite material films. For example, the morphology of an exemplary YBCO/Au composite material film wherein 200 Å of Au and 2000 Å of YBCO are deposited at 800 °C by ICM sputtering on an exemplary MgO substrate is similar to the morphology depicted in FIGS. 1 and 2. FIG. 6 illustrates the T_c dependence on Au thickness for the exemplary YBCO/Au composite material films deposited on exemplary MgO substrates. Similar results were obtained for exemplary substrates such as STO and LAO, but with less gold required to completely suppress T_c. The J_c was observed to systematically decrease with increasing Au thickness. Note that in FIG. 6, T_s = 800 °C, wherein T_s is the YBCO deposition temperature (i.e. deposition of YBCO on the substrate). T_c is the critical temperature of the composite material film wherein measurement of T_c was made by direct electrical contact to the sample. P_{tot} = 400 μm of total pressure of the argon/oxygen gas mixture used (e.g. 50 parts argon and 50 parts oxygen) during YBCO deposition. *See* L.H. Allen et al., *Thin film composites of Au and* $YBa_2Cu_3O_{7-\delta}$, Appl. Phys. Lett., vol. 66(8), pp. 1003-1005 (20 February 1995), incorporated herein by reference in its entirety and for all purposes. *See* E.J. Cukauskas et al., *Role of hydrogen in the growth of* $Y_1Ba_2Cu_3O_7$ *on MgO substrates by off-axis magnetron sputtering*, Appl. Phys. Lett., vol. 61(3), pp. 1125-1127 (31 August 1992), incorporated herein by reference in its entirety and for all purposes. *See* L.H. Allen et al., *Thin Film Composites of Au and* $YBa_2Cu_3O_{7-\delta}$, IEEE Transactions on Applied Superconductivity (to be published in 1995--see Copy in appendix I attached hereto and incorporated herein), incorporated herein by reference in its entirety and for all purposes. *See* M.A. Fisher et al., *Thin Film Y-Ba-Cu-O/Ag Composites for Fluxonic Devices*, IEEE Transactions on Applied Superconductivity (to be published 1995--Copy in appendix I attached hereto and incorporated herein), incorporated herein by reference in its entirety and for all purposes. Note that the T_c is measured for exemplary YBCO/Au composite material films wherein the thickness of the Au puddles is 0 Å, 200 Å, 500 Å, 1000 Å and 2000 Å, respectively, for the five plots of resistance versus temperature depicted in FIG. 6.

FIG. 7 illustrates the change in voltage as a function of current due to an external applied magnetic field of 3 Gauss for an exemplary YBCO/Au composite material film at selected temperatures of 19 degrees Kelvin, 31 degrees Kelvin, 41 degrees Kelvin and 50 degrees Kelvin, respectively. The differential voltage plotted in FIG. 7 represents the I-V curve modulation due to an external control magnetic field. The magnitude of this voltage per unit change of magnetic field is a measure of the potential usefulness of the composite material film in the fabrication of three terminal and non-linear superconducting devices. The voltage modulation must be sufficiently above the background noise level for use in such devices. Of equal importance is the vortex velocity. Its origin must not be thermal in nature but related to electronic forces or re-distribution of circulating currents such as is the case for Josephson vortices. The superconductor/noble metal composites such as YBCO/Au and YBCO/Ag have characteristics useful in photodetector applications. There is a correlation between photoresponse and resistivity near T_c. Initially, there is a large drop in resistance as the exemplary YBCO grains of the exemplary YBCO/Au composites (see FIGS. 6 and 8) become superconducting and the photoresponse is predominantly bolometric in this resistive transition region. At lower temperatures (FIG. 6), a resistive foot or tail appears as the intergranular coupling becomes stronger with decreasing temperature. In this foot or tail of the resistivity, the photoresponse is due to bolometric and non-bolometric components. Finally, the resistance vanishes at the superconducting transition temperature and a zero resistance critical current develops with further reduction of temperature. These three regions correspond to distinctively different photoresponse characteristics of the composite material films.

The photoresponse of an exemplary YBCO/Au composite material film under several temperature and bias conditions was measured to demonstrate the responsiveness of these composite materials for photodetector applications. Operation in the superconducting region is non-thermal and may be used for high speed operation. These results are illustrated in FIG. 8 along with the resistance versus temperature characteristics of a 1 mm wide bridge by 1 mm long exemplary YBCO/Au composite material film. The film consisted of 500 Å of gold and 2000 Å of YBCO. The results were obtained using a He-Ne 2mW laser as the light source.

The novel composite material films have the essential properties required by several superconducting devices. The incorporation of a noble metal along the superconductor grain boundaries during deposition of the superconductor forms SNS junctions between the superconducting grains. By controlling the relative amounts (i.e. thickness) of the noble metal and superconductor, the intergranular coupling is controlled. The thickness control results in weak vortex pinning and greater vortex mobility with the application of an external magnetic field but without sacrificing high operating temperatures for devices. Additionally, the novel composite material films have high quality superconducting grains and clean interfaces at the boundary between the noble metal and superconductor as indicated by the high T_c of these materials (i.e. the T_c of the pure superconductor is not significantly decreased after formation of the superconductor/noble metal composite material film). These novel composite material films (i.e. of superconductor/noble metal) are ready, as deposited, for the fabrication of superconducting, three terminal, flux flow devices, as well as photodetectors and non linear, two terminal devices. *See* A.M. Kadin, *Duality of fluxonics in superconducting devices*, J. Appl. Phys., vol. 68(11), pp. 5741-5749 (01 December 1990), incorporated herein by reference in its entirety and for all purposes. *See* J.S. Martens et al., *Flux Flow Microelectronics*, IEEE Trans. Appl. Superconductivity, vol. 3, no. 1, pp. 2295-2302 (1993), incorporated herein by reference in its entirety and for all purposes. *See* Y.H. Kao et al., *Effects of silver doping in the high-T_c superconductor system Y-Ba-Cu-O*, J. Appl. Phys., vol. 67(1), pp. 353-361 (01 January 1990), incorporated herein by reference in its entirety and for all purposes. *See* F. Raissi et al., *Josephson fluxonic diode*, Appl. Phys. Lett., vol. 65(4), pp. 1-3 (03 October 1994), incorporated herein by reference in its entirety and for all purposes.

Having described the invention, the following examples are given to illustrate specific applications of the invention, including the best mode now known to perform the invention. These specific examples are not intended to limit the scope of the invention described in this application.

Examples

Substrates such as MgO which are hygroscopic in nature, the substrates (e.g. MgO) are stored in mineral oil. Prior to the use of an exemplary MgO substrate, the substrate must be cleaned to remove mineral oil and any particulate matter present upon the substrate. For removing the mineral oil and removing particulate matter the substrate may be cleaned according to the following procedure (I):

(1) clean substrate for 5 minutes in a trichloroethane (TCA) ultrasonic bath;

(2) then clean substrate again for another 5 minutes in a fresh TCA ultrasonic bath;

(3) then clean substrate for 5 minutes in a fresh methanol ultrasonic bath;

(4) then clean substrate for 30 minutes in a fresh methanol ultrasonic bath;

(5) then blow dry the substrate under nitrogen gas;

(6) then heat the substrate to about 1000 °C in pure oxygen for 12 hours at 1 atmosphere pressure of oxygen;

(7) then allow substrate to cool to ambient (e.g. room temperature) temperature.

For substrates that are not hygroscopic or not stored in mineral oil, the substrates may be cleaned according to the following procedure (II):

(1) clean substrate in boiling methanol for 2 minutes;

(2) then clean substrate in boiling isopropyl alcohol for 2 minutes;

(3) then blow dry the substrate in nitrogen gas.

Procedure (I) was used to clean MgO substrates and procedure (II) was used to clean STO substrates. In procedure (I), TCE (trichloroethylene) may be used instead of TCA; however, TCE is believed to be more toxic than TCA. Thus, use of TCA in procedure (I) is preferred.

Example 1

We prepared sample OA-449 by first cleaning an MgO substrate. We attached the substrate onto a substrate holder (a stainless steel disk of 3 inches in diameter and 1/4 inch in thickness) by the use of an exemplary silver paste (e.g. "Silver Paste Plus" from SPI Supplies, Inc., West Chester, Pennsylvania) between the substrate and the substrate holder and loaded the sample into our off-axis sputter system. We then sputtered (using conventional on-axis geometry) a 2000 Å thick Ag layer at ambient temperature. We heated the Ag sample to the optimal off-axis sputtering growth temperature for YBCO (670 °C) and annealed at 670 °C for 90 minutes, and the Ag film coalesced into islands. We then deposited an 850 Å thick film of YBCO onto the sample by off-axis sputtering. The YBCO was deposited in a chamber containing a $P_{tot} = 250\mu m$ total pressure of argon gas, oxygen gas and hydrogen gas (i.e. 62 parts argon, 38 parts oxygen and 12 parts hydrogen). The sample was cooled and removed from the vacuum chamber.

Example 2

We prepared sample OA-465 exactly as sample OA-449, except we used a 30 minute anneal and deposited 2132 Å of YBCO.

Example 3

We prepared sample OA-493 exactly as sample OA-449 except 3250 Å of Ag was deposited and 800 Å of YBCO was deposited.

Example 4

We prepared sample ICM-161C by cleaning an MgO substrate. We thermally evaporated a 500 Å thick layer of Au at ambient temperature in a separate evaporator vacuum chamber. We then attached the substrate to a substrate holder (using silver paste--"Silver Paste Plus" from SPI, Inc., West Chester, Pennsylvania) and loaded the sample into our inverted cylindrical magnetron (ICM) sputtering system. The Au sample was heated to the optimal growth temperature for ICM sputtering, 800 °C, and annealed for 15 minutes at 800 °C. We then deposited a 2000 Å thick layer of YBCO by ICM sputtering. The sample was cooled and removed from the chamber.

Serial No.:
Inventors: Cukauskas et al.

PATENT APPLICATION
Navy Case No. 76,340

ABSTRACT

The presently claimed invention is direct to a process of making a noble metal and superconductor composite material and the noble metal and superconductor composite material itself.

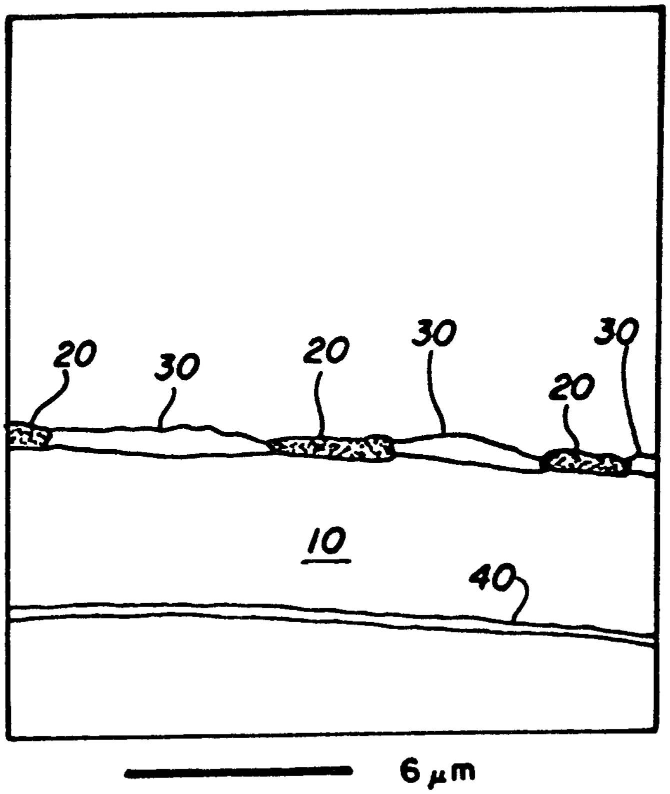


FIG. 1

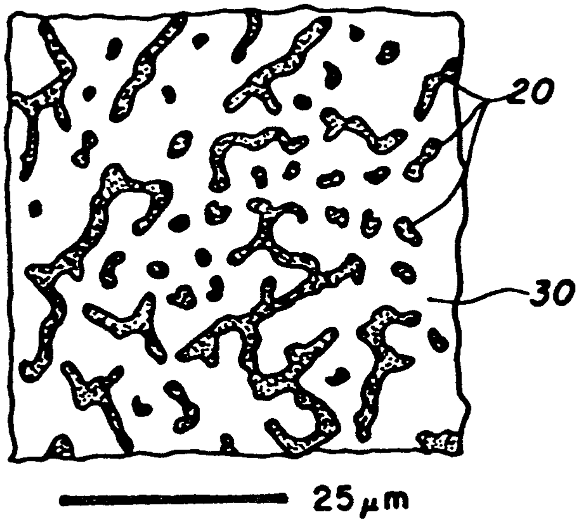


FIG. 2

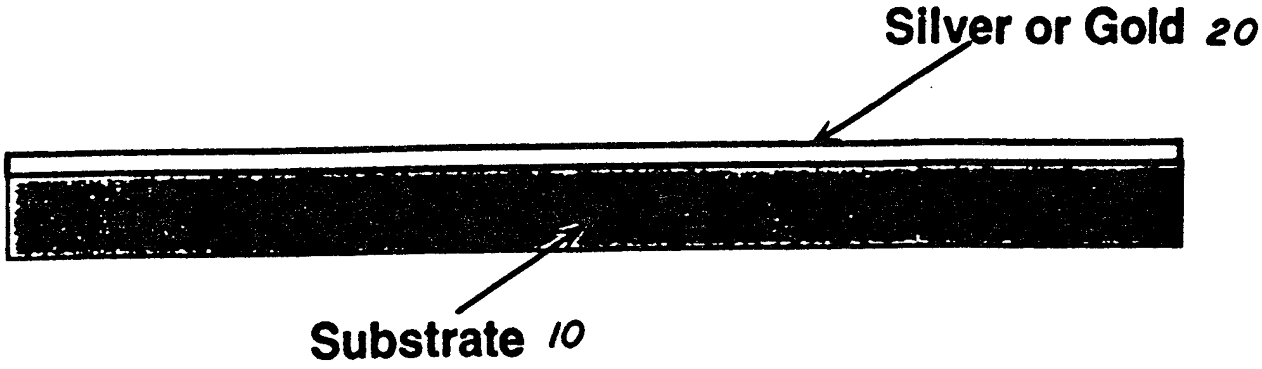


FIG. 3(a)

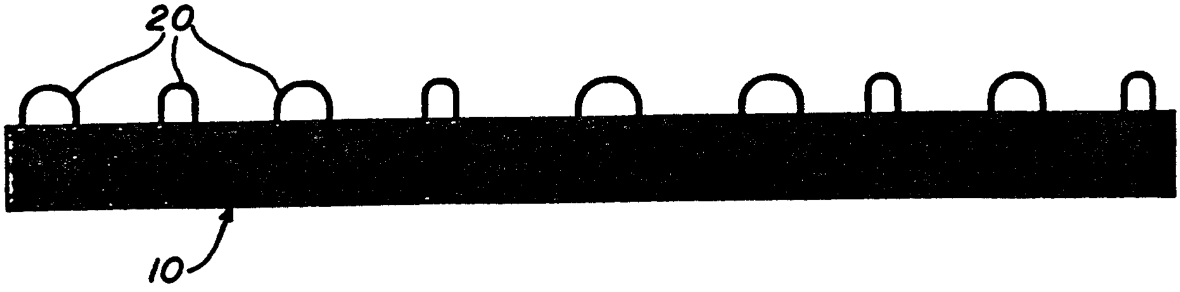


FIG. 3(b)

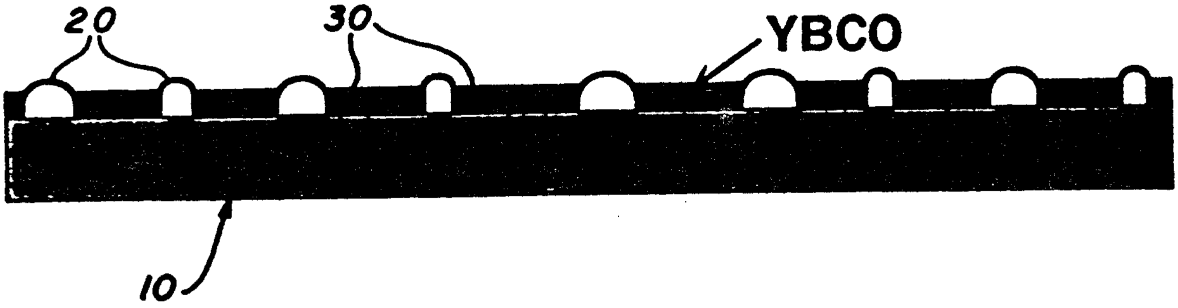


FIG. 3(c)

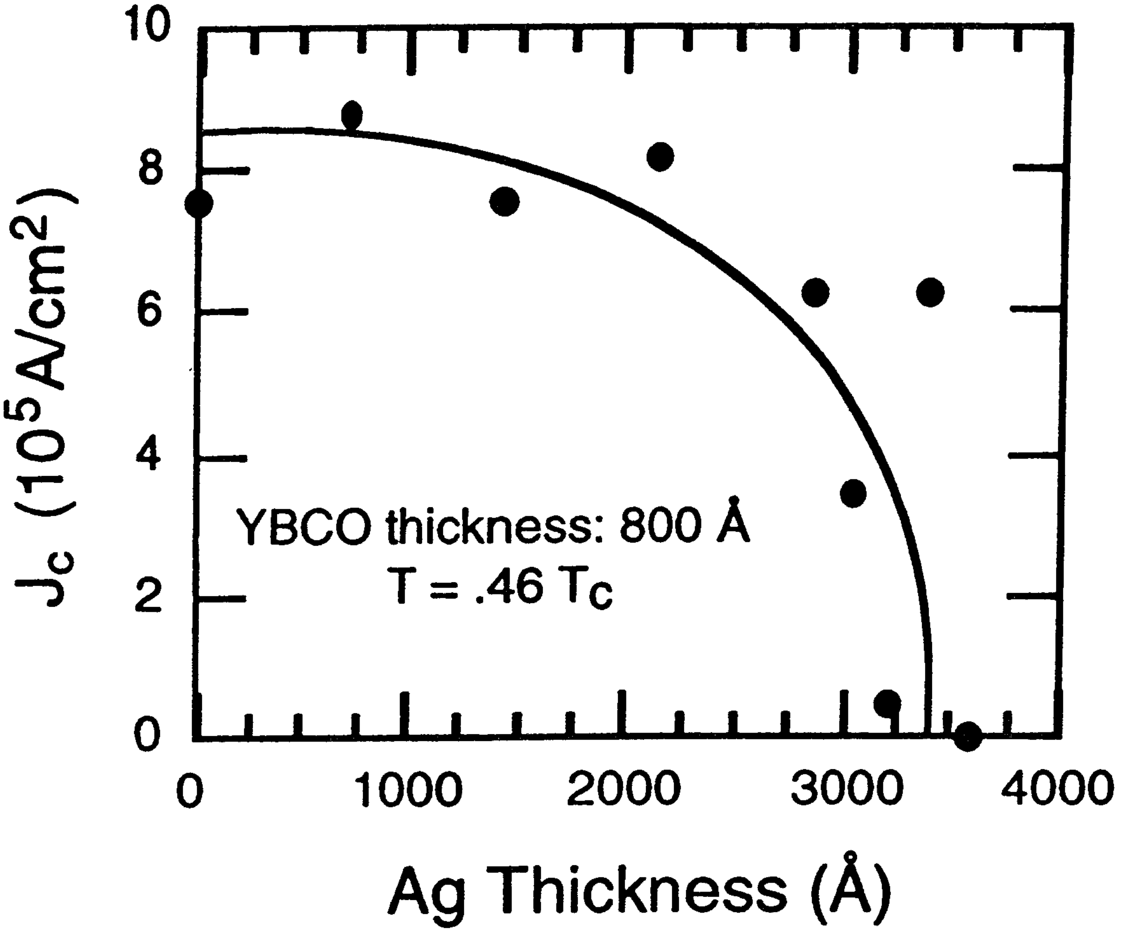


FIG. 4

J_c for composites with 800 Å of YBCO and various thicknesses of Ag. J_c is greatly reduced with increasing Ag thickness.

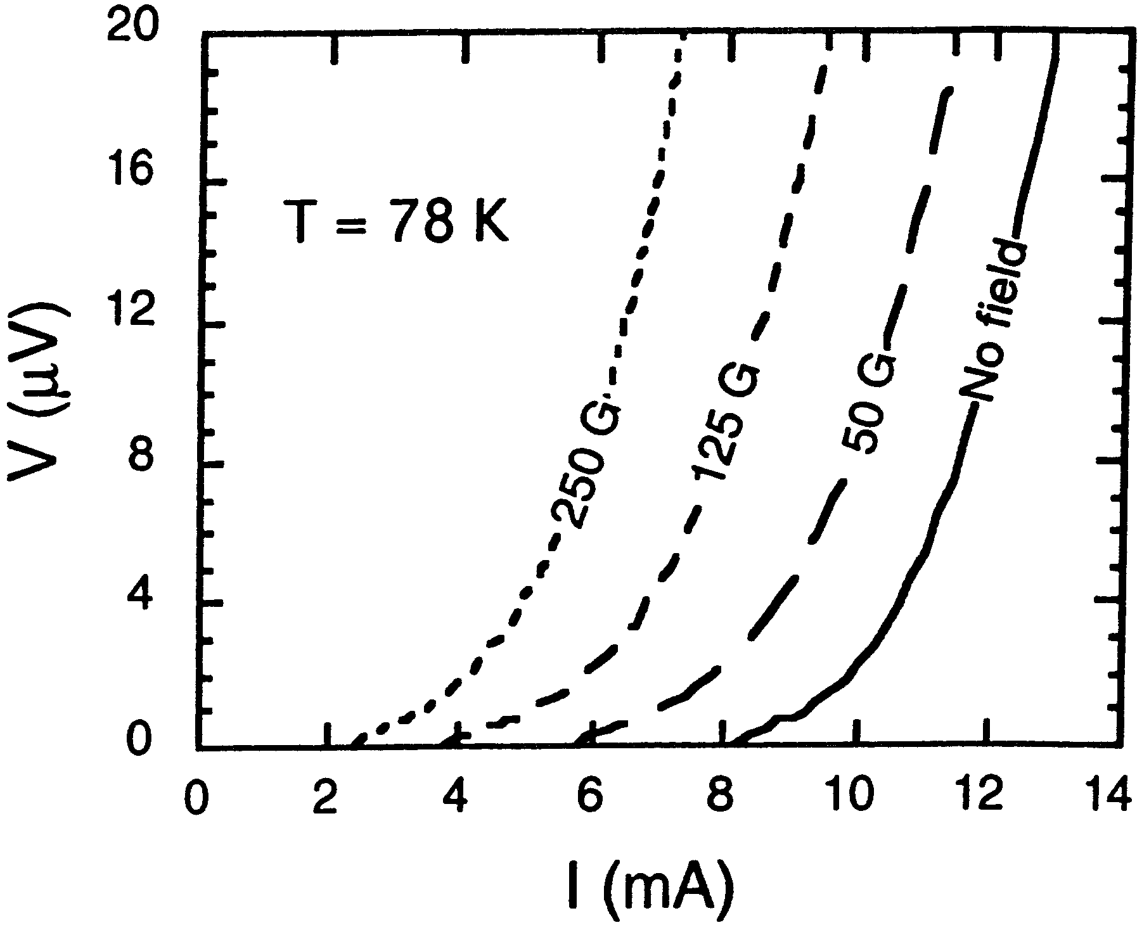
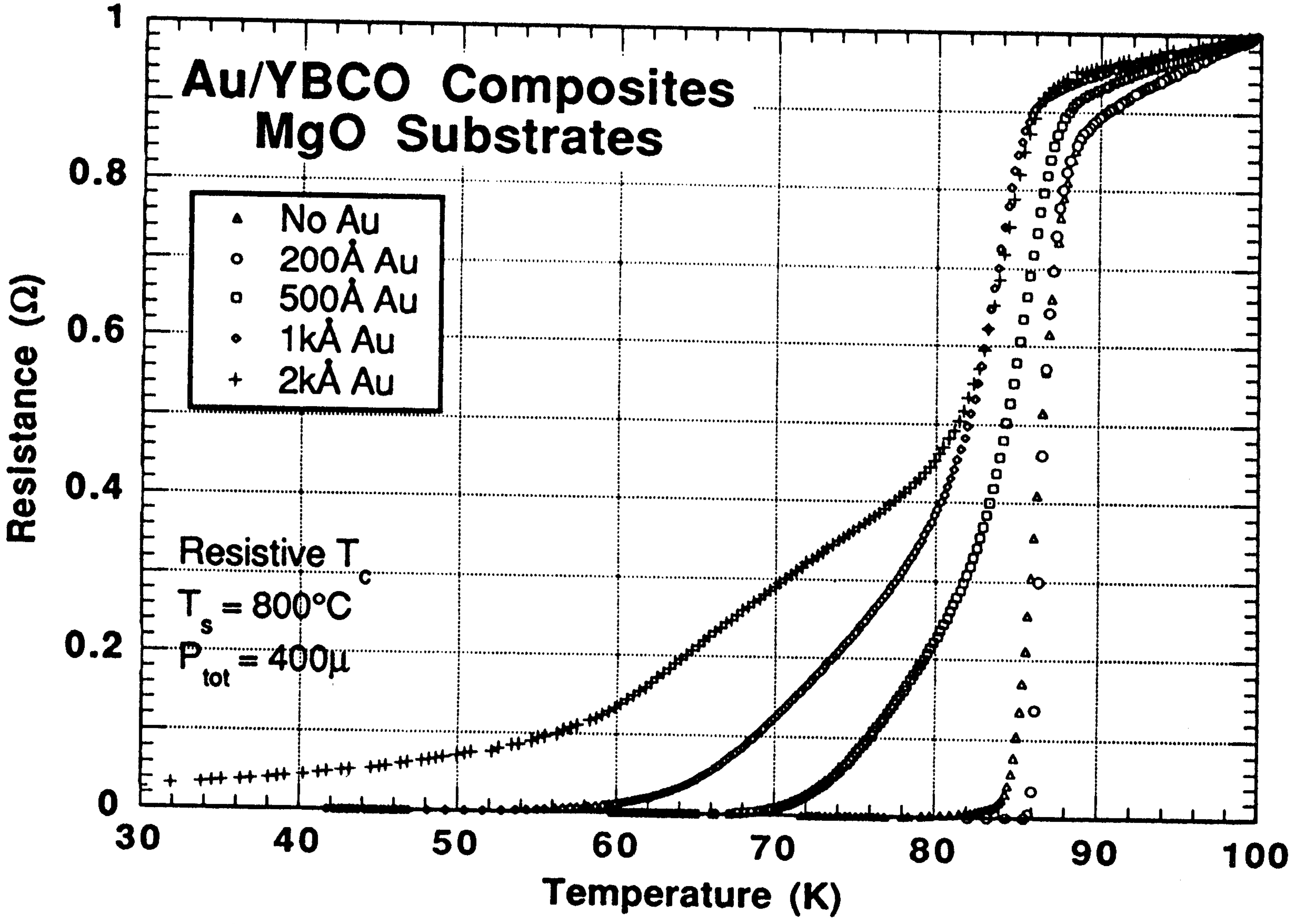


FIG. 5

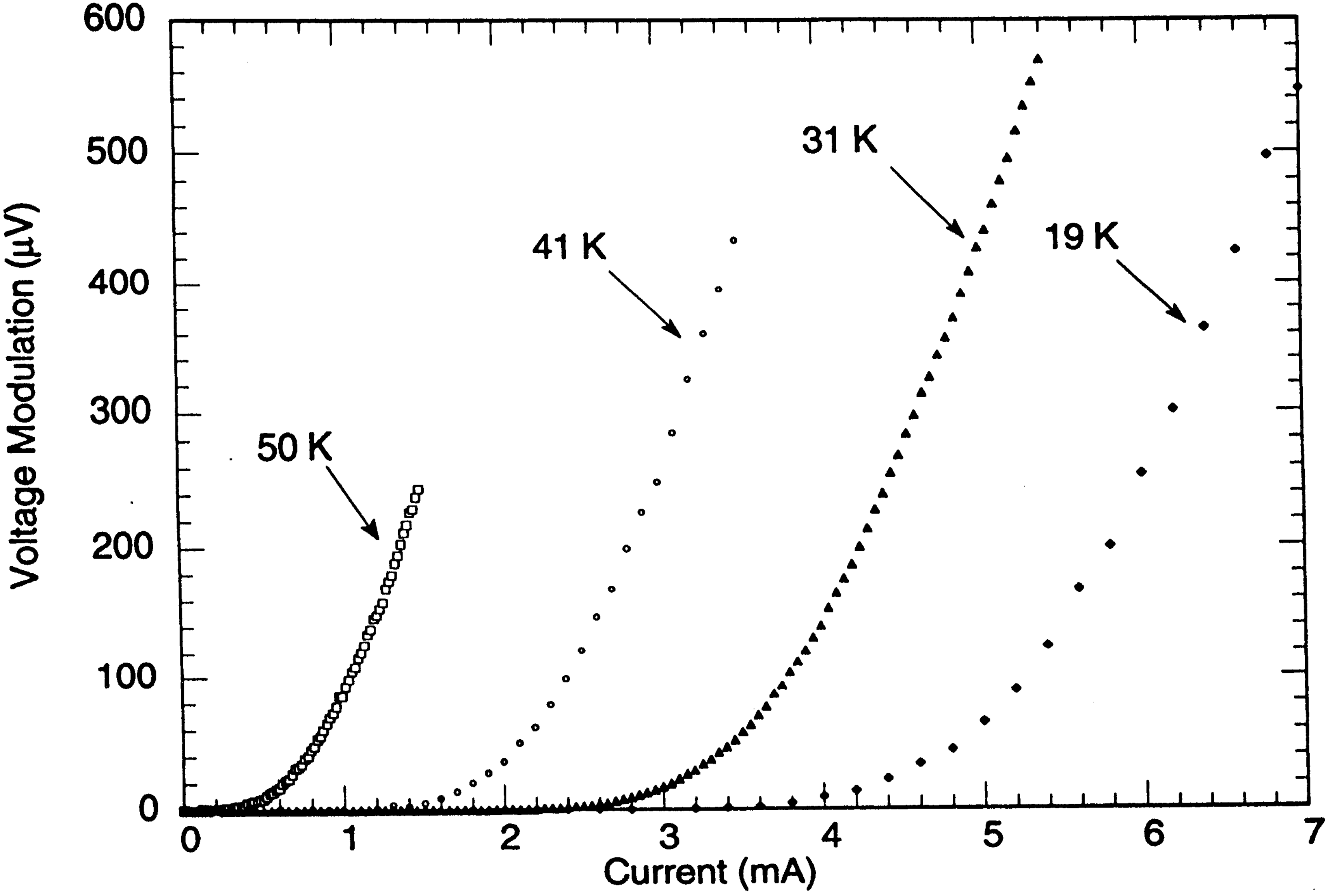
I-V traces for composite with 840 Å Ag, 800 Å YBCO. Small, applied fields cause significant reduction in J_c and increase in sample voltage at a given current.

FIG. 6



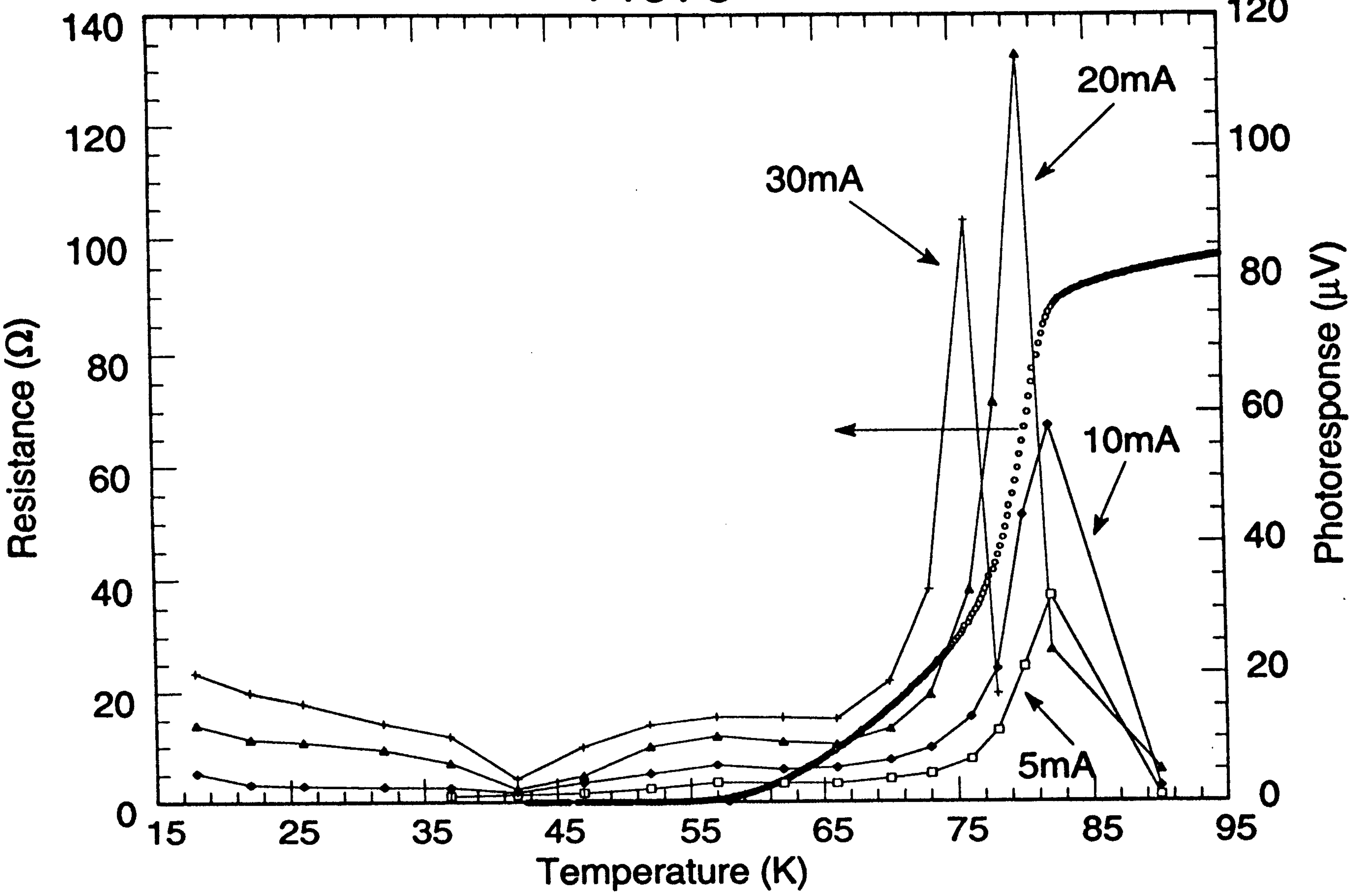
Resistive T_c's for Au/YBCO composites. The onset remains high, but tails get longer as Au layer thickness is increased.

FIG. 7



The voltage variation of a YBCO/Au composite bridge due to a 3 Gouss applied field at selected temperatures.

FIG. 8



The photoresponse and resistive transition of a YBCO/Au composite thin film bridge. The bridge bias current is indicated.

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Thin Film Y-Ba-Cu-O/Ag Composites for Fluxonic Devices

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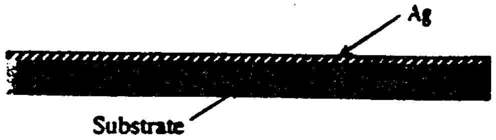
Abstract—We have investigated thin film composites of $YBa_2Cu_3O_{7-\delta}$ (YBCO) with Ag for fluxonic device applications. YBCO/Ag composite films are produced by first depositing a layer of Ag onto a substrate and then heating the film to the YBCO deposition temperature of 670°C or higher. YBCO is deposited by off-axis sputtering onto the Ag-coated substrate. The Ag migrates and segregates into distinct island-like regions several microns in size at these temperatures, and the resulting YBCO/Ag film is a composite of well-defined regions of Ag and YBCO. Scanning electron micrograph (SEM) images of the films' surfaces show a background of smooth YBCO grains dotted with Ag clusters. For a wide range of increasing Ag composition, the transition temperatures (T_c's) of the YBCO/Ag films remain high, while the critical current densities (J_c's) have been reduced as much as 65 times. On certain substrates, such as MgO, J_c's are also significantly suppressed in external magnetic fields of less than 5 mT. These measurements suggest that the composite films may be arrays of SNS junctions formed by weakly coupled YBCO grains with Ag in the grain boundaries. By varying the amount of Ag in the composites, we can "tune" the coupling of the YBCO grains. The field sensitivity and low J_c's of these composites make them potentially useful for development of flux-flow and fluxonic devices.

(a) Deposition of silver layer:



(b) Heating of sample causes puddling of metal

(c) Deposition of YBCO:

Fig. 1. Composite deposition process. Ag is deposited at room temperature. The substrate is then heated to approximately 700°C for the YBCO deposition.

I. INTRODUCTION

Superconducting thin films with low critical current densities (J_c's) and high sensitivity to magnetic fields are desirable for the fabrication of certain two-terminal and three-terminal devices. The fluxonic junction diode and the fluxonic junction transistor proposed by Kadin [1] rely on the motion of vortices and require a material with weak flux trapping or pinning forces. In the flux-flow transistor developed by Martens [2], the voltage across a superconducting bridge is modulated with an applied magnetic field from a nearby control line. Its active region must be composed of a material with a strong response to external fields.

Bulk composites of $YBa_2Cu_3O_7$ (YBCO) and silver have shown a reduction in J_c while retaining a high transition temperature (T_c) [3], [4]. We have been developing a thin film version of this class of composites, which exhibits similar electrical transport behavior. Preliminary analysis of the temperature dependence of critical current density indicates that the films consist of weakly coupled superconducting grains separated by narrow, normal regions. Josephson vortices are believed to be the most important magnetic flux carriers in the material, which may be, in effect, a non-uniform array of Josephson junctions.

II. SAMPLE PREPARATION

The films were deposited as two separate layers of Ag and YBCO and, at the elevated deposition temperature of the YBCO, formed the YBCO/Ag composite. The Ag was deposited onto a room temperature substrate. When the substrate was heated to approximately 700 °C for the YBCO deposition, the Ag migrated and coalesced into distinct islands. As the YBCO was deposited onto the array of Ag islands, the superconductor grew onto the exposed substrate and did not cover the Ag. This process is illustrated in Fig. 1. The resulting composite exhibited well segregated superconducting and normal regions. Composite films were grown on (100) MgO and $SrTiO_3$ (STO) substrates with Ag layers ranging in thickness from 0 Å to 5500 Å. The YBCO layers, 800 Å to 930 Å in thickness, were deposited by our standard, off-axis sputtering process [5] at a substrate temperature of 670 °C or 700 °C, depending on the sample.

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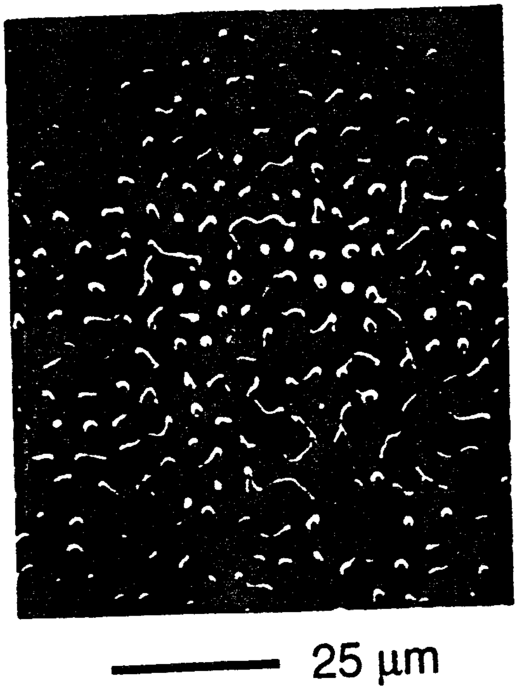

Fig. 2. Top view of YBCO/Ag composite on MgO with 850 Å of YBCO and 2000 Å of Ag. Note the well-defined and segregated YBCO and Ag regions.

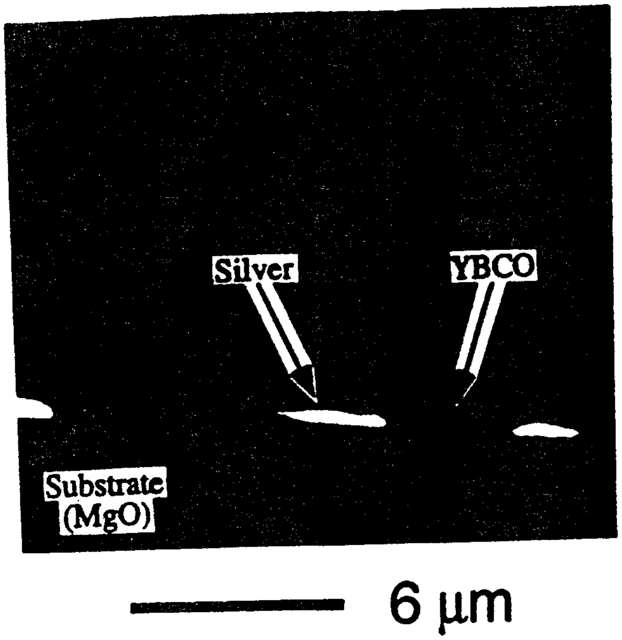

Fig. 3. Edge view of composite film. The dark areas of the film are YBCO and the light areas are Ag. The segregation of the YBCO and the Ag extends completely through the film, from the surface to the substrate.

III. STRUCTURAL CHARACTERIZATION

A. Scanning Electron Microscopy (SEM)

Fig. 2 shows a surface SEM of a composite with 850 Å of YBCO and 2000 Å of Ag on MgO. Energy dispersive spectroscopy has identified the dark regions as YBCO and the light regions as silver. The grains of Ag and YBCO have segregated from each other, but are closely connected, with no gaps between them. The segregation of the YBCO and noble metal regions extends through the entire thickness of the film, from the surface to the substrate. This is illustrated in Fig. 3, which shows a micrograph of a Ag composite sample which was cleaved in order to study the cross-section. Thinner Ag layers result in YBCO regions that are more well connected to each other, and thicker Ag layers produce normal regions that are more well-connected.

The interesting rectangular geometry of the Ag regions in Fig. 2 is characteristic of the Ag composites grown on MgO. This morphology has not been observed with composites deposited on STO substrates. On STO the Ag regions are also well segregated from the YBCO regions, but are irregularly shaped.

B. X-Ray Diffraction Studies

The crystalline structure of the composite films was studied using CuK_α radiation and an automated diffractometer with independent theta and two-theta. The Ag grains are polycrystalline and show no preferred ordering. The YBCO grains in films deposited at 670°C on MgO show a mixture of a-axis and c-axis orientations. In films grown at 700°C on STO the YBCO grains are predominantly c-axis oriented. Fitting the (00ℓ) peak positions to determine the c-axis lattice parameter (c_0), we find very little expansion of c_0 for the composites. Measurements have been made correlating c-axis lattice expansion with oxygen deficiencies in YBCO films [6], [7]. From this we conclude that our Ag composite films are well oxygenated.

IV. ELECTRICAL CHARACTERIZATION

A. General Transport Characteristics

We studied the effect of increasing Ag thickness on the electrical transport properties of composites deposited on both MgO and STO. T_c, transition width (ΔT_c), resistance ratio (RR), J_c at several temperatures, and room-temperature sheet resistance were determined for each sample. T_c was defined as that temperature for which the measured resistance became less than 1 mΩ. ΔT_c was defined as the temperature range in which the sample resistance changed from 10% to 90% of the normal state value immediately above the transition. RR was defined as the ratio of the film resistance at 295 K to the resistance at 100 K.

For the J_c measurements, the films grown on MgO substrates were scribed to form bridges approximately 2 mm wide and 1 mm long. The samples grown on STO were patterned lithographically into bridges 1 mm wide and 1.5 mm long. For determining the critical current of each sample, a voltage criterion of 1 µV was used. The calculation of J_c from I_c used the thickness of the YBCO layer and did not

TABLE I
SUMMARY OF ELECTRICAL PROPERTIES OF YBCO/Ag COMPOSITE FILMS ON MgO, WITH 800 Å OF YBCO

Ag (Å)	T_c (K)	ΔT_c (K)	RR	$R_\square$ (Ω/□)	J_c (77K, A/cm^2)
0 (typ.)	88	1.5	2.9	28	1.2×10^6
2000	85	2.2	2.3	41	5.88×10^4
2250	85	2.4	2.3	71	3.88×10^4
2500	84	2.3	2.4	35	4.75×10^4
3000	84	2.7	2.2	44	3.19×10^4

TABLE II
SUMMARY OF ELECTRICAL PROPERTIES OF YBCO/Ag COMPOSITE FILMS ON STO, WITH 930 Å OF YBCO

Ag (Å)	T_c (K)	ΔT_c (K)	RR	$R_\square$ (Ω/□)	J_c (t=0.9, A/cm^2)	n
0	87.5	1.3	2.6	116	3.66×10^5	1.55
1000	85.1	1.9	2.6	105	2.88×10^5	1.93
2000	84.7	2.0	2.3	156	1.71×10^5	1.74
3000	85.9	1.2	2.1	129	1.46×10^5	1.61
3500	80.7	3.0	1.8	132	2.29×10^4	1.90
4000	82.2	2.9	1.7	118	5.65×10^3	1.82
4170	—	—	1.73	35.2	—	—
4350	—	—	1.74	29.8	—	—

include the thickness of the Ag layer. The results for films on MgO are summarized in Table I and those for films on STO are summarized in Table II. The reduced temperature (t) is defined as T/T_c. Also shown in Table II is the power law exponent (n) of the temperature dependence function for J_c, which is explained further in section IV, part B.

Fig. 4a shows the dependence of J_c at several temperatures, as well as T_c, on Ag content for samples deposited on MgO. Reductions in J_c have been achieved without greatly degrading T_c. These results are preliminary and do not yet indicate how much Ag can be added to the films, and how much J_c can be reduced, before the T_c is significantly decreased.

Fig. 4b shows the corresponding results for samples deposited on STO. Little effect is seen until the Ag thickness exceeds 3000 Å, at which point J_c begins to drop rapidly, vanishing suddenly for Ag thicknesses between 4000 and 4200 Å. T_c remains high until this point, above which no complete transition is seen. At a reduced temperature of t = 0.9, the film with 4000 Å of Ag had a J_c 65 times lower than the film with no Ag. Further reductions in J_c might be achieved by approaching more closely the Ag thickness for which the material is no longer completely superconducting.

B. Intergranular Coupling

The J_c reduction may result from weakened trapping of Josephson vortices in the grain boundaries while Abrikosov vortices within the grains remain pinned. It is our hypothesis that the noble metal segregates into the YBCO grain boundaries, forming an array of SNS junctions with sharp interfaces between the superconductor and the normal metal. Although many of the normal regions seen in the SEM images appear to be over 1 μm in width, tunneling is possible through Ag barriers of this size, as has been observed by Tarte, et al [8]. More Ag increases the YBCO grain separation and weakens the intergrain coupling. Because the interface is preserved, the T_c is not degraded, and a composite with a thick Ag layer exhibits vortex motion at a lower current density than does a film with less Ag.

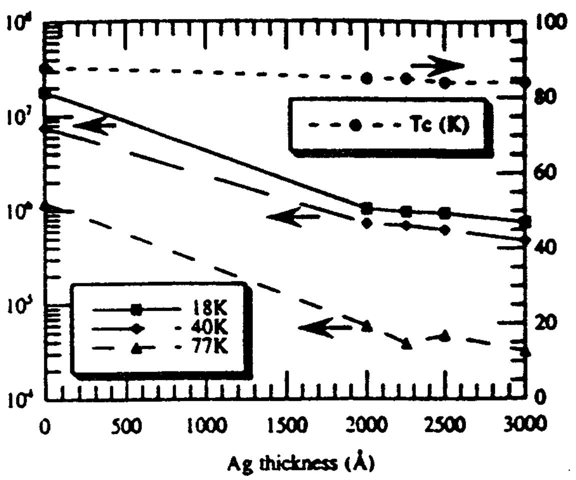

Fig. 4a. J_c and T_c for composites on MgO with 800 Å of YBCO and various thicknesses of Ag.

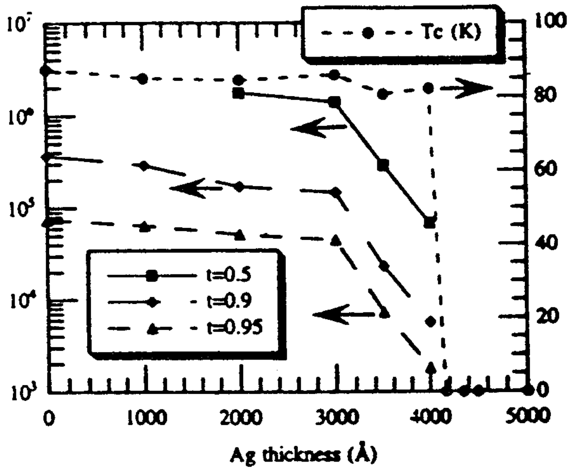

Fig. 4b. J_c and T_c for composites on STO with 930 Å of YBCO and various thicknesses of Ag.

In order to test this hypothesis, the temperature dependence of J_c in the composites was studied. Critical currents of films grown on STO were measured over the reduced temperature range from t = 0.9 to t = 1. The function $J_c = K\,(T_c - T)^n$, where K is a constant and n is the power law dependence of J_c on T, represents the behavior typically seen in superconducting samples near T_c. For a sample with characteristics dominated by SIS coupling between grains, the Ambegaokar and Baratoff theory should be applicable and n should equal 1, whereas for SNS or SS'S coupling, n=2 [9], [10], [11]. Some YBCO samples, however, have been

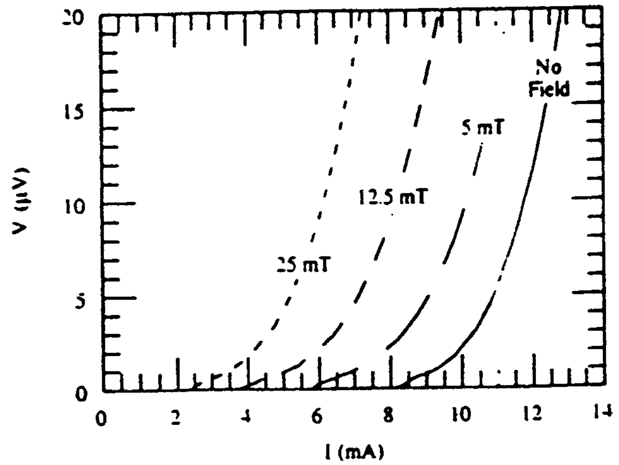

Fig. 5. I-V traces in magnetic fields for composite with 800 Å of YBCO and 840 Å of Ag on MgO (T = 77 K).

observed experimentally to follow the Ginzburg-Landau theory, which gives n=1.5 in the dirty limit [11], [12], [13], [14], [15].

A numerical curve fit to the function was performed, in which K, T_c and n were varied. Table 3 shows n as a function of Ag thickness, based on the results of the curve fitting procedure. The film with no Ag appears to exhibit Ginzburg-Landau behavior, having a power law exponent of 1.55. The films with added silver all have larger values of n, some as high as 1.9. This may be an indication that transport between a significant fraction of the grains is due to SNS coupling, with the silver serving as the normal metal.

Weak intergrain coupling in the Ag composites is further evidenced by the effect of small magnetic fields on their electrical properties. Fig. 5 shows the I-V curves for a composite bridge on MgO having 840 Å of Ag and 800 Å of YBCO. The low magnetic fields of 5, 12.5, and 25 mT applied perpendicular to the substrate cause significant I_c reduction from the value at ambient field and, over a range of currents, result in a substantial voltage response.

V. CONCLUSIONS

We have produced YBCO/Ag composite thin films with varying amounts of Ag. Segregation of the YBCO and the Ag into distinct regions occurs during the deposition of the YBCO. The Ag regions are observed to be more well-connected, and the YBCO regions correspondingly less well-connected, in samples with larger amounts of silver. The superconducting and normal regions of films grown on MgO exhibit a regularly spaced, rectangular morphology, whereas the features of films grown on STO are irregular in shape.

Studies of the electrical characteristics of the materials have demonstrated reductions of J_c by a factor of 65 at t = 0.9 without greatly degrading T_c. Near T_c the J_c's of the composites follow a power law dependence on the difference between T_c and the measurement temperature. Addition of large amounts of Ag result in a power law exponent greater than 1.8, which may indicate that many of the grains are SNS coupled.

The films on MgO exhibit a significant voltage response to small magnetic fields. Less effect is apparent for samples on STO. It is possible that the effect of substrate type on electrical transport in magnetic fields may be related to the observed differences in morphology between the films grown on MgO and those grown on STO.

The greatly reduced critical current densities of YBCO/Ag composites, as well as their sensitivity to magnetic fields, indicate that, with further optimization, these materials show promise for the fabrication of flux-flow and fluxonic junction devices.

ACKNOWLEDGMENT

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REFERENCES

[1] A. M. Kadin, "Duality and fluxonics in superconducting devices," *J. Appl. Phys.*, vol. 68, pp. 5741-5749, 1990.
[2] J. S. Martens, V. M. Hietala, T. A. Plut, D. S. Ginley, G. A. Vawter, C. P. Tigges, M. P. Siegal, J. M. Phillips, and S. Y. Hou, "Flux flow microelectronics," *IEEE Trans. Appl. Superconductivity*, vol. 3, pp. 2295-2302, 1993.
[3] J. Jung, M. A.-K. Mohamed, S. C. Cheng, and J. P. Franck, "Flux motion, proximity effect, and critical current density in $YBa_2Cu_3O_{7-\delta}$/silver composites," *Phys. Rev. B*, vol. 42, pp. 6181-6195, 1990.
[4] Y. H. Kao, Y. D. Yao, L. Y. Jang, F. Xu, A. Krol, L. W. Song, and C. J. Sher, "Effects of silver doping in the high-T_c superconductor system Y-Ba-Cu-O," *J. Appl. Phys.*, vol. 67, pp. 353-361, 1989.
[5] E. J. Cukauskas, L. H. Allen, G. K. Sherrill, and R. T. Holm, "Role of hydrogen in the growth of $Y_1Ba_2Cu_3O_7$ on MgO substrates by off-axis magnetron sputtering," *Appl. Phys. Lett.*, vol. 61, pp. 1125-1127, 1992.
[6] E. Sodtke, C. Andrzejak, D. Guggi, and Y. Xu, "Preparation of a-axis oriented $YBa_2Cu_3O_7$ and $PrBa_2Cu_{3-x}Ga_xO_7$ thin films," *Physica C*, vol. 180, pp. 50-53, 1991.
[7] J. Q. Zheng, M. C. Shih, S. Williams, S. J. Lee, H. Kajiyama, X. K. Wang, Z. Zhao, K. Viani, S. Jacobson, P. Dutta, R. P. H. Chang, J. B. Ketterson, T. Roberts, R. T. Kampwirth, and K. E. Gray, "Effect of oxygen partial pressure on the *in situ* growth of Y-Ba-Cu-O thin films on $SrTiO_3$," *Appl. Phys. Lett.*, vol. 59, pp. 231-233, 1991.
[8] E. J. Tarte, H. W. Lean, Z. H. Barber, J. R. Waldram, R. E. Somekh, "The proximity effect between YBCO and silver," *Physica C*, vol. 185-189, pp. 2575-2576, 1991.
[9] V. Ambegaokar and A. Baratoff, "Tunneling between superconductors" (Errata), *Phys. Rev. Lett.*, vol. 11, pp.104,105, 1963.
[10] G. Deutscher and K. A. Müller, "Origin of superconductive glassy state and extrinsic critical currents in high-T_c oxides," *Phys. Rev. Lett.*, vol. 59, pp. 1745-1747, 1987.
[11] S. Greenspoon and H. J. T. Smith, "Study of the superconducting proximity effects by Josephson tunneling," *Can. J. Phys.*, vol. 49, pp. 1350-1360, 1971.
[12] N. L. Rowell and H. J T. Smith, "Investigation of the superconducting proximity effect by Josephson tunneling," *Can. J. Phys.*, vol. 54, pp. 223-226, 1976.
[13] J. Clarke, "Supercurrents in lead-copper-lead sandwiches," *Proc. R. Soc.* (London), vol. A308, pp. 447-471, 1969.
[14] J. W. C. de Vries, M. A. M. Gijs, G. M. Stollman, T. S. Baller, and G. N. A. van Veen, "Critical current as a function of temperature in thin $YBa_2Cu_3O_{7-\delta}$ films," *J. Appl. Phys.*, vol. 64, pp. 426-429, 1988.
[15] J. Aponte, H. C. Abache, A. Sa-Neto, and M. Octavio, "Temperature dependence of the critical current in high-T_c superconductors," *Phys. Rev. B*, vol. 39, pp. 2233-2237, 1989.

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Thin Film Composites of Au and $YBa_2Cu_3O_{7-\delta}$

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Abstract—We are using a novel bilayer deposition process to grow composite films of Au with $YBa_2Cu_3O_{7-\delta}$. The composites have well-separated regions of Au and $YBa_2Cu_3O_{7-\delta}$, and we see no evidence for structural or chemical degradation of the grains and grain boundaries. For composite films on MgO substrates, the transport properties indicate the presence of weakened superconductivity in the films. Composites on $SrTiO_3$ and $LaAlO_3$ do not show this as strongly. The MgO composites behave like arrays of Josephson junctions and show promise as materials for flux flow devices.

I. INTRODUCTION

There has been considerable interest recently in superconducting flux flow and fluxonic devices [1], [2]. These devices are based on the motion of either Abrikosov or Josephson vortices and require a material whose properties do not impede the flow of magnetic flux. The high pinning strengths of $YBa_2Cu_3O_{7-\delta}$ (YBCO) have made it unsuitable for flux flow devices without modifying the YBCO in some manner such as thinning it [3] or taking advantage of naturally occurring defects such as the grain boundary junction formed over a substrate step [4].

We have been working on an alternative approach to this problem: finding a material that consists of a random array of Josephson junctions in which Josephson vortices can move easily throughout the film. This material will "as-grown" have the desired property of easy flux motion, avoiding extra steps for device processing. Composite systems of YBCO with the noble metals, Au and Ag, have properties that suggest the material forms an array of Josephson junctions [5], [6]. We have developed a novel "bilayer" technique for making thin film composites of YBCO with Au and Ag and are studying their characteristics for flux flow applications. In this paper, we report the effects of varying the amount of noble metal in thin film composites of Au with YBCO and the use of different substrates.

II. FILM PREPARATION

A novel "bilayer" deposition process was used to grow the composite films. First, the Au layer was thermally evaporated onto the cleaned substrates at ambient temperatures. As deposited, the Au films were smooth and shiny. Next, the samples were silver-pasted onto a substrate holder and heated for the YBCO deposition. At the YBCO growth temperature (800 °C), the Au film coalesced into islands on the substrate surface, and the deposited YBCO filled in the regions between the Au islands. The YBCO was grown by inverted cylindrical magnetron sputtering using deposition conditions that reproducibly yield films with resistive T_c's in the 85 K range and J_c's of 10^6 A/cm^2 or higher at 77 K [7].

III. MORPHOLOGY

We have studied the morphology of our composite films using x-ray diffraction (XRD) and scanning electron microscopy (SEM). Fig. 1 is a SEM micrograph of a composite film with 200 Å of Au and 2 kÅ of YBCO. As indicated by Energy Dispersive Spectroscopy (EDS), the light-colored, irregularly-shaped regions are Au grains, and the dark background area is YBCO grains. We see no indication of mixing or alloying between the Au and YBCO in SEM micrographs or in the XRD spectra. We cleaved a composite sample and examined the film's cross section with the SEM (not shown). From that, we find that the Au regions extend from the substrate interface to above the film surface,

Fig. 1. SEM micrograph of the surface of a Au/YBCO composite. The light regions are Au, and the dark background YBCO.

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TABLE I

TRANSPORT MEASUREMENTS FOR Au/YBCO COMPOSITES ON MgO SUBSTRATES

Au Thickness (Å)	Before Pattern T_c (K)	After Pattern T_c (K)	ρ at 100 K ($\mu\Omega$-cm)	RR	J_c at 30 K (A/cm^2)	J_c at 50 K (A/cm^2)	J_c at 77 K (A/cm^2)
0	84.0	83.6	440	2.4	8.3×10^5	4.6×10^5	5.6×10^4
200	83.7	82.8	810	2.3	2.2×10^6	1.2×10^6	6.4×10^4
500	62	53	1900	1.4	1.5×10^3	1.9×10^2	-
1000	35	21	3300	1.2	-	-	-
2000	incomplete	incomplete	490	1.2	-	-	-

looking very much like mountain plateaus. The YBCO grains form channels which fill in between the Au clusters. With thicker Au layers, the number of YBCO channels decreases, but the channel dimensions and the Au cluster size do not change much. A thin, wetting Au layer appears to form at about 2 kÅ of Au, the thickest Au layers we tried.

For all these films, the YBCO grains are mostly c-axis oriented and the Au grains predominantly (111)-oriented. Analyzing the c-axis peak locations, we see no lattice constant expansion, indicating that the grains are fully oxygenated [8] and that Au atoms are not being incorporated into the YBCO lattice [9]. Full-width-half-maximums of the YBCO (007) rocking curves show a small, but systematic increase with thicker Au layers indicating an increase in the YBCO grain disorder.

These characterizations lack the resolution to identify structures which could be Josephson junctions. The Au clusters are too large for Josephson tunneling to occur at these temperatures (40 K and higher) [10]. Another possibility is the grain boundaries. However, to the extent that we can see, the YBCO grains and boundaries in the composites have the same appearance and properties as those of our best YBCO films.

IV. TRANSPORT MEASUREMENTS

Ag contact pads were evaporated onto the samples to study the transport properties of the Au/YBCO composites. We cooled the samples in a closed-cycle helium refrigerator and measured the temperature dependence of the resistance to obtain the transition temperature T_c (here used to mean the zero resistance temperature) and the resistance ratio RR between room temperature and 100 K. Some films were patterned into a bar geometry using standard photolithographic methods and a wet chemical etch (dilute HCl acid) to test the effects of processing and to obtain the resistivity and critical current density J_c. The dimensions used to calculate the resistivities and J_c's were the dimensions of our pattern and YBCO layer thickness. We realize that these dimensions are inaccurate in that they fail to account for the complicated transport distribution in the composite films. Despite this uncertainty, the values obtained are useful for comparisons.

A. Au Thickness Dependence

A series of composites with a 2 kÅ thick YBCO layer and Au layers varying from 200 to 2 kÅ thick were grown on (100) MgO substrates. T_c's, RR's, resistivities, and J_c's were measured, and the results summarized in Table I. The resistive transitions are also plotted in Fig. 2, normalized to their value at 100 K. A "plain" 2 kÅ thick YBCO film is included for comparison. As the Au thickness is increased, the onset of the transition remains high and a tail develops in the resistance, becoming longer for more Au. Grain boundary weak links in YBCO films on MgO substrates have been correlated with tails in the resistive transitions [11]. Table I shows that the resistivities are increasing (except for the 2 kÅ Au composite where the Au layer is probably shorting out the YBCO) and RR's are decreasing for increasing Au in the composites. This trend has also been observed for bulk Au composites, and attributed to increased grain boundary resistance from Au precipitates [9].

After patterning, the J_c's were also measured. Some representative values are shown in Table I. The data are limited, but the large decrease in J_c between the 200 and 500 Å Au composites suggests that an important change is occurring in the material. To study this further, we measured the temperature dependence of J_c for these films and fit the data near T_c to a power dependence

$$J_c \propto (1 - t)^n$$

where t is the reduced temperature, T/T_c. Our "plain" YBCO films follow the 3/2 power dependence predicted by Ginzburg-Landau theory for thin films, as does the 200 Å Au composite. However, the 500-Å Au film follows a linear dependence, which is predicted for arrays of Josephson-coupled grains in the superconducting/insulating/-superconducting limit [12]. Further evidence for Josephson coupled grains was seen by measuring I-V curves for the 500-Å Au film in ambient and very small magnetic fields. We observed that a perpendicular magnetic field of 3 Gauss pro-

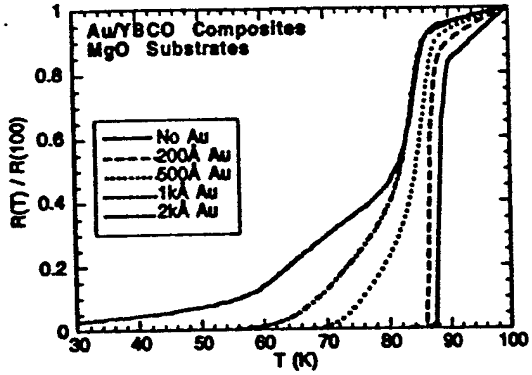

Fig. 2. Normalized temperature dependence of the resistance of composite films with various amounts of Au. With increasing Au thickness, the onset remains high, but a tail develops.

TABLE II

TRANSPORT MEASUREMENTS FOR Au/YBCO COMPOSITES ON DIFFERENT SUBSTRATES

Film	Before Pattern T_c (K)	Before Pattern RR	Before Pattern ΔT_c (K)	After Pattern T_c (K)	After Pattern RR	After Pattern ΔT_c (K)	ρ at 100 K ($\mu\Omega$-cm)
Composite on $SrTiO_3$	86	2.4	1.0	81	2.0	1.6	5.0×10^{-4}
Composite on $LaAlO_3$	86	2.4	0.7	84	2.2	1.3	3.0×10^{-4}
Composite on MgO	~40	1.5	12.	~20	1.2	21.	9.2×10^{-4}
Control on $SrTiO_3$	83	2.7	3.	84	2.7	0.7	1.9×10^{-4}
Control on MgO	82	2.4	1.4	85	2.7	1.3	1.4×10^{-4}

duced a 45% increase in the bar's voltage at a bias current of 5 mA at 30 K.

The transport data, then, indicates that the Au/YBCO composites on MgO substrates have regions of weakened superconductivity, and films with thicker Au layers have weaker coupling across these regions. At the same time, the normal state properties reflect increased grain boundary resistance. These observations are consistent with weakly-coupled YBCO grains in the composites, with the amount of Au in the composites affecting the coupling strengths.

B. Substrate Dependence

The effects of substrate choice on grain boundaries and transport properties of YBCO films are significant. If our composites are arrays of coupled Josephson junctions with the coupling occurring across the YBCO grain boundaries, then substrate choice should also significantly affect the composites' properties. To test this, we prepared three identical composites, changing only the substrate. The films were prepared at the same time, and (100) substrates of $SrTiO_3$, $LaAlO_3$, and MgO were used. The Au layer was 1 kÅ thick, and the YBCO layer 2 kÅ.

Table II is a summary of the T_c and normal state properties for these composites. Data are included for two YBCO control films grown on $SrTiO_3$ and MgO substrates. The transitions for the control samples are high and sharp, as for the composites on $SrTiO_3$ and $LaAlO_3$. As Table II shows, the transition for the composite on MgO differs, being lower and broader. Also, we observe that the RR's and resistivities are similar for these films: the composites on $SrTiO_3$ and $LaAlO_3$ are like the control films, but the composite on MgO is different. The trend with patterning is the same, little degradation for the control and composites on $SrTiO_3$ and $LaAlO_3$, but significant change for the composite on MgO.

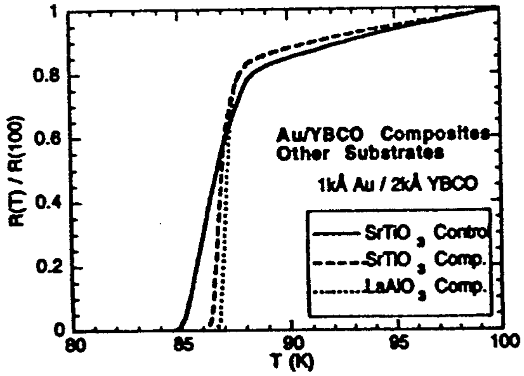

Fig. 3. Normalized temperature dependence of the resistance for identical composites grown on $SrTiO_3$ and $LaAlO_3$ substrates and a control YBCO film on $SrTiO_3$. Sharp, high transitions are different from transitions of the 1-kÅ Au composite on MgO shown in Fig. 2.

The J_c's of these films are given in Table III. Comparing the composite on $SrTiO_3$ with the control film on $SrTiO_3$, we see a factor or 10 decrease in J_c. The difference in J_c's of the composite and control on MgO is much greater. The effects of an applied perpendicular magnetic field were also measured. The last column in Table III is the ratio of J_c at 135 Gauss to the ambient field J_c at 77K. Again, the results for the composites on $SrTiO_3$ and $LaAlO_3$ are similar to the controls.

The Au composites on $SrTiO_3$ and $LaAlO_3$ substrates do not have the same signs of weakened superconductivity that the composites on MgO have. They are more similar to plain YBCO films. Perhaps the better match of these substrates to the YBCO lattice and the avoidance of rotated YBCO grains that grow on MgO substrates [11] are responsible for this. Our present results indicate that for flux flow applications, the MgO composites appear to be the most promising materials.

V. CONCLUSIONS

We have developed a novel bilayer deposition technique for growing thin film composites of Au with YBCO. The composites consist of irregularly shaped "islands" of Au in a background of YBCO grains. XRD and SEM studies suggest that the YBCO grains have the same characteristics as the grains in good c-axis YBCO films. The transport properties, however, indicate that the superconductivity in composites on MgO substrates is significantly weakened, while composites on $SrTiO_3$ and $LaAlO_3$ are less affected. The properties of the MgO composites are consistent with the material being an array of Josephson-coupled junctions, with the coupling determined by the amount of Au in the composite. These composites show promise for flux flow device materials.

TABLE III

J_c's FOR COMPOSITES ON DIFFERENT SUBSTRATES

Film	J_c at 15 K (A/cm^2)	J_c at 77 K (A/cm^2)	$\frac{J_c \text{ at 135 Gauss}}{J_c \text{ at ambient at 77K}}$
Composite on $SrTiO_3$	1.5×10^6	3.8×10^4	0.65
Composite on $LaAlO_3$	2.7×10^6	1.9×10^4	1.
Composite on MgO	10	–	–
Control on $SrTiO_3$	1.2×10^7	8.0×10^5	0.75
Control on MgO	1.5×10^7	1.0×10^6	0.82

REFERENCES

[1] G. K. G. Hohenwarter, J. S. Martens, J. H. Thompson, J. B. Beyer, and J. E. Nordman, "Characteristics of superconducting flux-flow transistors", *IEEE Trans. Magn.*, vol. 27, pp. 3297-3300, March 1991.

[2] A. M. Kadin, "Duality and fluxonics in superconducting devices", *J. Appl. Phys.*, vol. 68, pp. 5741-5749, December 1990.

[3] J. S. Martens, G. K. G. Hohenwarter, J. B. Beyer, J. E. Nordman, and D. S. Ginley, "S-parameter measurements on single superconducting thin-film three-terminal devices made of high-T_c and low-T_c materials", *J. Appl. Phys.*, vol. 65, pp. 4057-4060, May 1989.

[4] J. S. Martens, et al., "Flux flow microelectronics", *IEEE Trans. Appl. Super.*, vol. 3, pp. 2295-2302, March 1993.

[5] D. Veretnik and S. Reich, "Nonrandom gold-$YBa_2Cu_3O_{7-x}$ Composites", *J. Appl. Phys.*, vol. 73, pp. 8429-8435, June 1993.

[6] Y.H. Kao, et al., "Effects of silver doping in the high-T_c superconductor system Y-Ba-Cu-O", *J. Appl. Phys.*, vol. 67, pp. 353-361, January 1990.

[7] L. H. Allen, E. J. Cukauskas, G. K. Sherrill, R. T. Holm, and P. K. Van Damme, "Sputtered thin films of $Y_1Ba_2Cu_3O_{7-x}$ on MgO substrates", in *Advances in Cryogenic Engineering (Materials)* vol. 38, F. R. Fickett and R. P. Reed, Eds. New York: Plenum Press, 1992, pp. 1019-1025.

[8] W. R. McKinnon, et al., "Oxygen intercalation in the perovskite superconductor $YBa_2Cu_3O_{6+x}$", *Phys. Rev. B*, vol. 38, pp. 6543-6551 October 1988.

[9] M. Z. Cieplak, et al., "Incorporation of gold into $YBa_2Cu_3O_7$: structure and T_c enhancement", *Phys. Rev. B*, vol. 42, pp. 6200-6208, October 1990.

[10] A. Barone and G. Paterno, *Physics and Applications of the Josephson Effect*, New York: John Wiley & Sons, 1982, pp. 161-169.

[11] S.E. Russek, et al., "Weak link properties of $YBa_2Cu_3O_{6+\delta}$ thin film grain boundaries", in *Science and Technology of Thin Film Superconductors 2*, R.D. McConnell and R. Noufi, Eds. New York: Plenum Press, 1990, pp. 331-340.

[12] V. Ambagaokar and A. Baratoff, "Tunneling between superconductors", *Phys. Rev. Lett.* vol. 10, pp. 486-489, June 1963; and errata vol. 11, p. 104(E), July 1963.