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TITLE HIGHLY-TEXTURED THALLIUM-BARIUM-CALCIUM-COPPER-OXIDE POLYCRYSTALLINE SUPERCONDUCITNG FILMS ON SILVER SUBSTRATES.

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HIGHLY-TEXTURED Tl-Ba-Ca-Cu-O POLYCRYSTALLINE SUPERCONDUCTING FILMS ON Ag SUBSTRATES

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ABSTRACT

Thick (8 to 10 μm) Ba-Ca-Cu-O films have been rf magnetron sputtered onto Ag alloy (Consil 995) substrates. The films were given a post-deposition anneal in an over pressure of Tl in order to form the superconducting phases. Annealing protocols were done which result in predominantly the 1212 and 2212 phases. The substrate orientation was varied to determine its effect on film orientation. Material properties of the films were characterized by x-ray diffraction (XRD), ion beam backscattering spectroscopy, energy dispersive x-ray analysis (EDAX), and scanning electron microscopy (SEM). Electrical characterization of the films was done using dynamic impedance (DI) at 10 kHz and rf surface resistance (R_s) at 18 GHz in a TE_{011} fundamental mode cavity.

INTRODUCTION

High-temperature superconducting (HTS) materials have potential practical application in rf and microwave accelerating cavities.[1] This application requires that relatively large-area substrates (10^2 - 10^3 cm^2) be used which have good thermal conductivity to the coolant medium. Further, the substrate material must be capable of: being shaped or machined into non-planar geometries; having good bonding properties; being resistant to oxidation at elevated temperatures; and having minimal deleterious effects on the electrical properties of the HTS material. In a few instances, these stringent requirements are met by Pt[2] and Au.[3] However, other work shows both of these elements to be deleterious to the superconducting properties.[4] Silver has been more frequently used as a substrate material or in combination with HTS systems with no deleterious effects detected.[4,5,6,7,8] Also, it is far less expensive than the former metals. Consil 995 is an age-hardenable alloy of Ag as well as having increased strength at high temperatures.[9] Its composition is 99.5% Ag, 0.25% Ni, and 0.25% Mg.

Film deposition on large areas is practical using a variety of techniques which include organometallic chemical vapor deposition,[5,10] plasma spraying,[11] or sputter deposition.[12,13] This work uses rf magnetron sputtering from a single oxide target of Ba-Ca-Cu-O. The Tl is introduced in a post-deposition annealing step when the HTS phases are formed.

Using these sputtered oxide precursor films, anneal protocols were varied to determine the parameter space needed to obtain predominantly c-axis oriented Tl-based HTS films on rolled Consil substrates. In the second phase of this work, this information was combined with variations in substrate orientation to optimize materials properties of the final films. Finally, the surface resistance of a 38 mm diameter film on a rolled Consil substrate (the most facile method for metallic substrate preparation) is measured.

EXPERIMENTAL PROCEDURES

A metal oxide target of the nominal $Ba_2Ca_1Cu_2O_x$ composition was used in a 10 cm diameter rf magnetron sputter gun. Substrates were placed 35 mm from the target on a planetary style (dual-axis) rotator. During deposition, as many as five 38 mm diameter substrates may be coated simultaneously. Deposition conditions are input power=1.7 W/cm^2, deposition rate=8 nm/min, film thickness=0.8×10^4 to 1.0×10^4 nm, and sputter gas composition-partial pressures of $Ar/O_2 = 8 \times 10^{-3}/4 \times 10^{-3}$ torr. The background plasma heats the substrates to over 200 °C during deposition. Ion beam backscattering spectroscopy showed the cation composition of the films to be within 10% of the composition of the target. The substrates used were either ~1 cm^2 for comparative studies in materials and DI characteristics, or were 38 mm in diameter for materials characterization and R_s measurements.

The post-deposition annealing apparatus used to generate the Tl over pressure has been described previously.[14] Annealing temperatures varied from 885 to 910 °C. The dwell times at these temperatures were also varied from a few minutes up to thirty minutes. Several 1 cm^2 films could be annealed simultaneously but only one of the 38 mm diameter films could be annealed at a time.

The effect of substrate texture on the orientation of the HTS film was considered. If the lattice spacing of the substrate can be made an integral multiple of the HTS film a-axis, preferential c-axis orientation of the film should be enhanced. In the case of cubic Ag, several choices exist. Rolling of Consil produces predominantly (220) texturing with lattice spacing differing by 12.6% from that of the Tl HTS a-axis. Drawing of Consil produces predominantly (200) texturing which results in a 6.2% difference. These two cases plus an as cast, unoriented Ag substrate were examined to determine the effect of substrate texture on film orientation. (311) or (331) substrate textures would also result in comparable lattice matching but were not pursued.

Films of Tl superconductor (1 cm^2) were prepared simultaneously on the three substrate types. They were then characterized by XRD, ion beam backscattering, EDAX, SEM, and DI. A 38 mm diameter film on rolled Consil was also produced for this study so that an 18 GHz R_s measurement could be obtained in addition to the other materials characterizations.

The temperature dependent R_s of the large-area film was measured using an end wall replacement technique, which is described in a previous paper.[15] Briefly, the cavity is a cylinder operating in the fundamental TE_{011} mode. One of the end walls is replaced with a HTS superconducting film. The R_s of the film is then computed from the change in the cavity quality factor (Q) caused by the replacement.

The DI technique is similar to ac susceptibility measurements. However, the DI technique uses only one inductive coil and measures its out-of-phase (inductive) component at a set drive frequency caused by the coupling between the coil and the supercurrents induced in the film.[16] This information correlates to the onset of supercurrents in a superconducting film as a function of temperature. This technique also provides a relative measure of the amount of material which gets converted into the superconducting state. Currently, the DI measurements can only be done on films whose diameters are ≤ 25 mm.

RESULTS

Using rolled Consil substrates, it was found that predominantly c-axis orientation of the HTS films occurs only when a threshold temperature is reached during the anneal cycle. For a dwell time of two minutes, XRD showed the film structure to be unoriented if the maximum temperature was 885 °C, or less. This is illustrated in Figure 1a. If the maximum anneal temperature was increased to 890 °C, then XRD showed (Figure 1b) the films to have a predominantly c-axis orientation. For both films, a ramp-up and ramp-down rate of 16 °C/min was used. Thus, orientation occurs relatively rapidly during the higher temperature anneal. SEM showed the unoriented films to be equiaxed with angular edges while the c-axis oriented films consist of flat tabular grains that are nominally parallel to the substrate surface. These plate like grains are rounded at the edges. This latter observation as well as the rapidity of anneal used implies that a liquidus state is attained during the higher temperature anneals which result in the c-axis films.

For the films deposited and annealed simultaneously on the three separate types of Consil substrates, an anneal time of thirty minutes was used. Figure 2 illustrates the XRD patterns of the three films. For these films the predominant HTS phase is 1212. A small amount of 2212 material is also found on the film on the cast substrate (Fig. 2a). All of the films have c-axis orientation. The abundance of favorable lattice matching orientations of Ag with the HTS basal plane makes even a cast unoriented Ag substrate likely

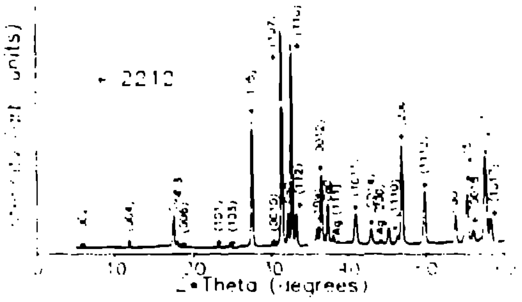


Fig. 1a Film annealed at 885° C

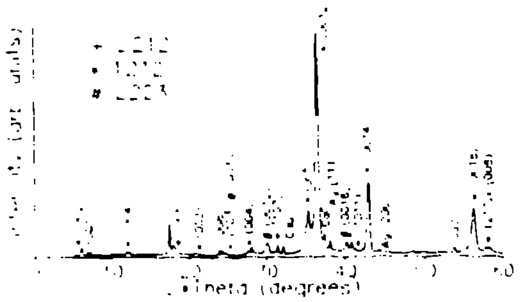


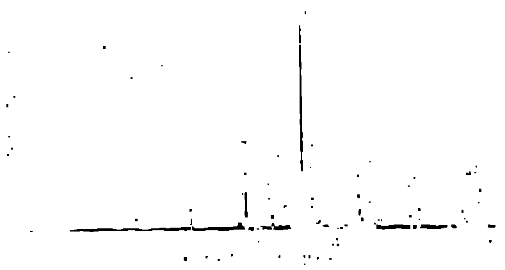
Fig. 1b Film annealed at 890° C

to produce HTS film orientation. It is seen that the peak intensities increase as the lattice match of the substrate with the HTS basal plane becomes more favorable. That is, the least to greatest peak 1212 intensities are for films on the cast, rolled, and drawn substrates, respectively. The non-HTS oxides found on all three substrates are CaO and Tl_2O. The intensities of these non-HTS oxides are approximately the same for the films on the drawn and cast substrates and slightly less for the film on the rolled substrate.

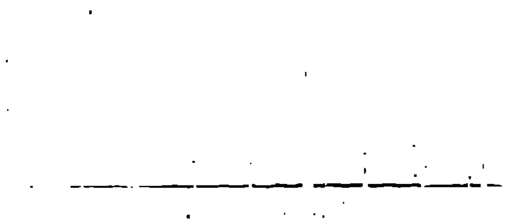
Note that the (00ℓ) peaks of the 1212 phase in figure 2 are narrower than those of the 2212 (00ℓ) peaks seen in figure 1b. Equally narrow (00ℓ) peaks have been seen on every 1212 textured film made to date in our program. The (00ℓ) peaks for non-1212 phases seen on other films made in this program have always been found to be wider than for the 1212 (00ℓ) peaks. This is attributed to fewer defects within the 1212 grains than those of other phases. Defects arise from the intergrowth of phases.[17] This implies that the 1212 phase lies at the left edge of a pseudo-binary phase diagram.[18]

SEM of the three films shows essentially the same features. As shown in figure 3a, the films consist of large (≥ 30 μm) flat tabular grains which appear to be fused together. Figure 3b shows concentrations of hemispheres which are also found on all three films. EDAX shows these hemispheres to be primarily calcium oxide. However, an occasional hemisphere is found to be primarily Ag. The specific gravity of calcia is roughly one-half that of the HTS material. Also, the melting point of calcia is more than twice that of the HTS material. Thus, it is not unreasonable to assume that it rises to the surface of the superconducting material during the liquidus portion of the anneal cycle. No reason can be advanced for the Ag globules found on the surface.

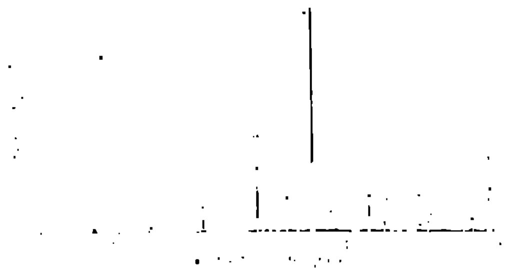
Using an electron probe beam energy of 25 keV, EDAX of the platelets shows them to be Tl-Ba-Ca-Cu-O material with no Ag detected. (The limits of detection for Ag are 0.1 to 0.5 wt.% for this technique.) Assuming a HTS density of 6.5 gm/cm^3, a Monte Carlo simulation of the penetration depth for 25 keV electrons is approximately 1.6 μm. Thus, (except for the distinct surface globules of Ag) the Ag has not diffused



(2a)



(2b)



(2c)

Fig. 2 X-ray diffraction patterns of three HTS films deposited and annealed simultaneously on three different substrates: (a) cast Consil, (b) rolled Consil, and (c) drawn Consil.

(3a)

(3b)

Fig 3. Scanning electron micrographs of annealed films on rolled Consil substrate. 3(a) shows the grains to be tabular with rounded edges. 3(b) shows a region where CaO hemispheres have congregated.

Figure 4 shows the spectra for high-energy (8.8 MeV) ion-backscattering from an as-deposited and annealed film. Also shown is a $Ba_2Ca_1Cu_2O_x$ simulation of the unannealed film. The as-deposited film spectrum indicates that some Ag diffusion has occurred during deposition of the oxides. The annealed film spectrum shows the Tl addition to the film as well as a greater degree of Ag diffusion into the film. A simulation of the spectrum which most closely fits the annealed films' backscattering data indicates the stoichiometry to be $Tl_{0.9}Ba_{1.8}Ca_{1.0}Cu_{2.0}O_8$. (This fit assumes the addition of the Tl has increased the film thickness to 11 μm and the atom density is 3.43 at/cm^3.)

The backscattering data provides a qualitative estimate of how near Ag is to the film surface. It is observed that the high-energy backscattering limit for Ag occurs at ≈6.6MeV. (This value would be 7.6 MeV for Ag at the surface.) A TRIM[19] (TRansport of Ions in Matter) calculation of the energy loss of the detected ions on their trajectories within the target suggests a corresponding scattering depth of ≈3 μm. There is, therefore, little or no Ag within approximately 3 μm of the film surface.

Dynamic impedance measurements of the films show all three to have transitions approximately 40 K wide. Other films whose XRD spectra exhibit weak orientation (e.g. for a 1212 film with (103) peak intensity 1/4 that of the (005) peak) show no transition at all using the DI method. As shown in figure 5, the 1212 film on the drawn substrate has a transition which starts at approximately 90 K. The film on the rolled substrate had a transition nearly identical to that of Fig. 5. The film on the cast substrate, which has a small amount of 2212 material has a transition which starts at 105 K. The relatively good quality of the XRD data for

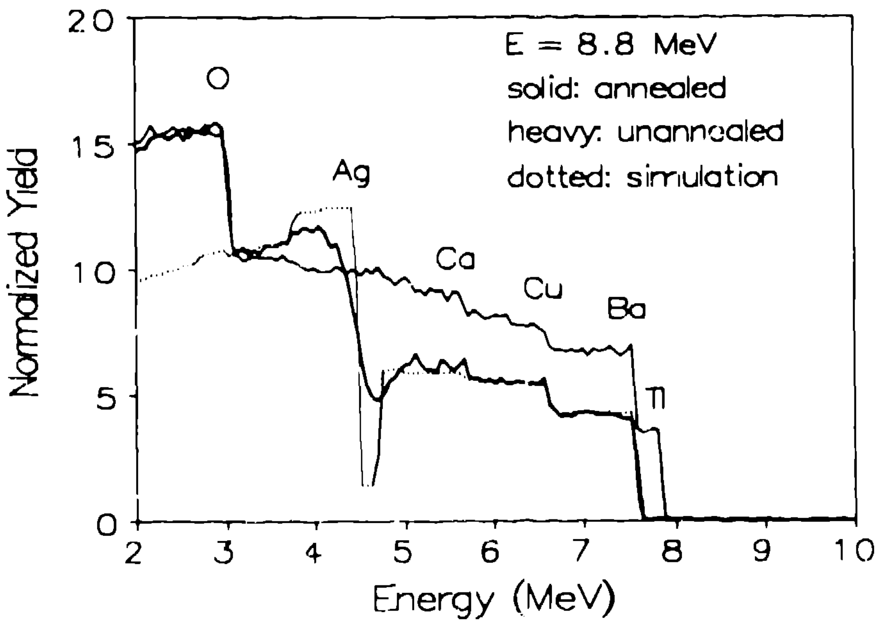


Fig 4. Backscattering spectra of unannealed and annealed film. Also shown is a simulation for an unannealed $Ba_2Ca_1Cu_2O_x$ film.

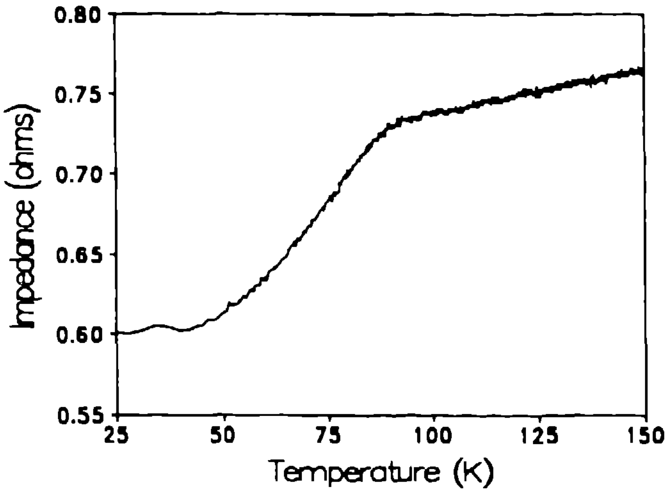


Fig. 5. Dynamic impedance measurement of a HTS film on a drawn Consil substrate.

these films makes the 40 K transition width seem rather high. These widths are attributed to the non-HTS material found on the surface by SEM.

A 38 mm diameter film was then prepared on rolled Consil in a fashion similar to the previous films. The annealing times were shortened in an attempt to reduce the amount of the non-HTS material on the film surface. Figure 6 shows the XRD spectrum for this film to be primarily c-axis oriented and predominantly the 1212 phase. The amount of non-HTS oxide is also much less than for the previous films. SEM showed the surface morphology of this film to be similar to that of the film illustrated in Fig. 3. However, EDAX shows the residual material seen on the surface of the large tabular grains to be primarily HTS rather than CaO. The non-HTS oxide that is found is $BaCuO_2$. The R_s vs. temperature of this film is shown in figure 7. The R_s for this film is 4.2 mΩ (@ 12 K, 18 GHz). This is the lowest value we have attained to date for large-area films on metallic substrates.

CONCLUSIONS

In summary, 11 μm thick superconducting films of Tl-Ba-Ca-Cu-O on Consil 995 have been prepared by rf magnetron sputtering from a compound target of Ba-Ca-Cu-O and annealing in a over pressure of Tl. The films become oriented with the c-axis predominantly perpendicular to the substrate surface if the anneal temperature is sufficiently high. The c-axis orientation is further improved if the substrate is textured so that its lattice spacing is nearly an integral multiple of that of the HTS basal plane. This occurs by two common metal processing techniques, rolling or drawing. SEM shows the c-axis oriented films to have attained a liquidus state during their annealing with some segregation of calcia to the surface of the films. Dynamic impedance shows the films to have comparable transition widths. Ion-beam backscattering shows the Ag to diffuse into the films. A TRIM calculation indicates that the Ag is no closer than ≈ 3 μm from the film

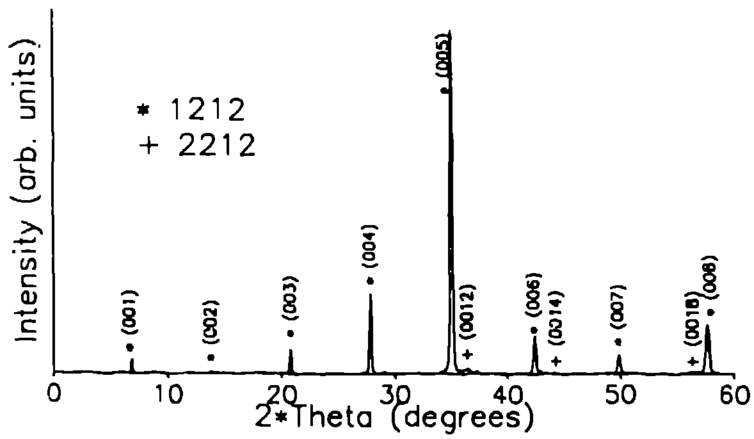


Fig. 6 X-ray diffraction spectrum of a 38 mm diameter HTS film on a rolled Consil substrate.

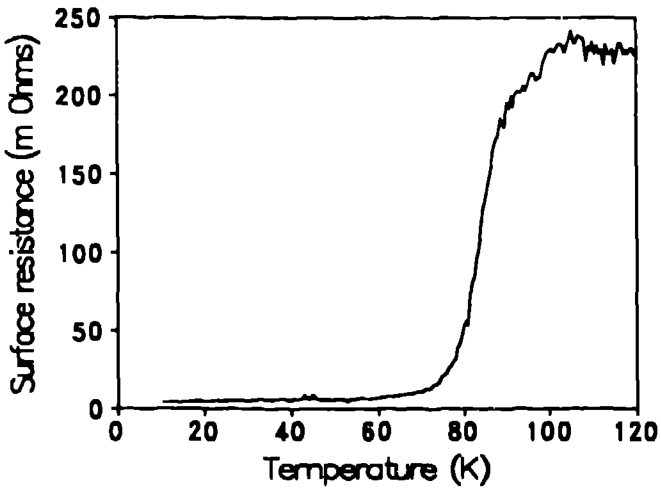


Fig. 7. Surface resistance versus temperature for a 38 mm diameter HTS film on a rolled Consil substrate.

surface. EDAX shows that the diffusion of Ag into the films does not come any closer than ≈1.6 μm from the surface. Surface resistance measurements of a 38 mm diameter highly-textured HTS film on rolled Consil yield a value of 4.2 mΩ at 18 GHz and 12 K.

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