THIN FILM PREPARATION AND SINGLE FILM DEVICE FABRICATION IN THE TL-CA-BA-CU-O HTS SYSTEM

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Superconducting polycrystalline thin films in the Tl-Ca-Ba-Cu-O system have been prepared by electron beam evaporation followed by appropriate sintering and annealing. Transition temperatures to 110 K and critical current densities to 600,000 A/cm^2 have been attained in oxygen annealed films. However, with only 16 minutes of air sintering and no oxygen anneal, oriented films have been obtained with T_c's to 107 K and J_c's to 450,000 A/cm^2. Single film devices utilizing a parallel array of weak links and a coplanar control line have been fabricated from the films. Oscillators as well as AM and FM modulators operating between 3 and 6 GHz have been demonstrated using this device concept.

The recent discovery of high temperature superconductivity in the Tl-Ca-Ba-Cu-O system [1,2] has produced a family of superconducting phases with T_c's over 100K [3,4]. The highest documented transition temperatures to date with T_c over 120K are typically found for the $Tl_2Ca_2Ba_2Cu_3O_{10}$ phase [5-7]. Interest in thin films is stimulated by the potential for applications. Recently, we reported randomly oriented 0.7 μm films of the $Tl_2CaBa_2Cu_2O_8$ phase obtained by e-beam evaporation [8] with a T_c (R=0) of 97K and a transport J_c of 1.1 x 10^5 A/cm^2 at 76K. We obtained similar results for the $Tl_2Ca_2Ba_2Cu_3O_{10}$ phase with T_c to 107K and Jc to 2.4 x 10^5 A/cm^2 at 76K [9]. Transport and magnetization data demonstrate essentially no effects due to weak links in appropriately processed films. However, flux pinning is very weak at 77K, suggesting the possibility of even higher critical currents in appropriately modified material [10-12]. Other groups have obtained oriented films of the $Tl_2CaBa_2Cu_2O_8$ and $Tl_2Ca_2Ba_2Cu_3O_{10}$ phases by various sputtering techniques [13-16]. Their results include T_c's to 120 K and J_c's to 10^5 A/cm^2 at 100K.

Thin Film Deposition and Characterization

The complex chemistry of the Tl-O system, as illustrated in equation 1,

$$Tl_2O_3 \leftrightarrow Tl_2O + O_2\uparrow \leftrightarrow 2Tl + O_2\uparrow \qquad \text{(eq. 1)}$$

involves the reversible loss of oxygen stepwise from the most oxidized species, Tl_2O_3, to the most reduced, Tl metal. The nature of the Tl species present during processing appears to dominate the granular and intergranular properties of the thin films. The point in the equilibrium phase diagram where processing is optimum is located on a multidimensional surface and will be a function of at least the temperature, oxygen partial pressure, thallium partial pressure and the effective volatility of the various Tl-O species at the interface between the solid and vapor. We present results showing how different sintering configurations can control morphology and the superconducting properties of thin films. We demonstrate how proper control of the Tl concentration during processing with very short air sintering times and no subsequent oxygen anneal can result in very high quality films. We have also obtained high quality superconducting films that are composed of mixed Tl phases indicative of the tolerance of this system to variable stoichiometries. These results illustrate the potential for scalable processing for Tl-Ca-Ba-Cu-O films.

Films are deposited by sequential electron beam evaporation. Under a slight oxygen overpressure (1-3 x 10^{-5} mbar, to prevent intermetallic phase formation) pure metals are evaporated onto the substrate of choice ($SrTiO_3$, Y-ZrO_2, MgO or sapphire with or without a coating of Y-ZrO_2). Evaporation is done in layers starting with Cu and ending with Cu to encapsulate the structure. Film of 0.3 μm, 0.7 μm and 1.5 μm thickness have been made using 12, 25 and 49 layers respectively. The average layer thicknesses to achieve a stoichiometry of $Tl_2Ca_2Ba_2Cu_3O_{10}$ (in the order deposited) are Cu: 159Å, Ba: 675Å, Ca: 450Å, and Tl: 298Å. The substrate temperature was kept below 50 C. The as deposited materials were metallic as expected, but showed no evidence of superconductivity. The resulting partially oxidized structures are sensitive to oxygen and moisture and are consequently stored in a dry box before sintering and annealing. Results presented here will focus on $SrTiO_3$ substrates; results on other substrates are analogous with respect to overall film quality and morphology.

Sintering is the most critical process in the formation of high quality films, although the substrate plays a significant role in defining the orientation of the films. In this process the film is fully oxidized and the Tl-based phases synthesized. The morphology of the film is also established at this time. Liquid Tl phases, perhaps Tl_2O, appear to be crucial to the formation of high quality grain boundaries. To date initial sintering in pure oxygen has not produced films with superconducting properties as good as those for air sintered films, presumably because liquid phase formation is suppressed.

Recent work has centered on the sintering configuration where the substrate sits on top of bulk $Tl_2Ca_2Ba_2Cu_3O_{10}$ ceramic while a second bulk $Tl_2Ca_2Ba_2Cu_3O_{10}$ ceramic is above but not in contact with the film ("free surface"). The sintering stack is placed in a lidded platinum crucible and the crucible is cycled to 850°C, held there for 15 min and rapidly cooled. The films investigated for this study were 0.3 μm and 0.7 μm thick. Comparable results were obtained for both thicknesses. The exact composition of the bulk ceramics used for the Tl source was found to be critical. A narrow window of compositions from $Tl_{1.96}$ to $Tl_{2.04}$ produced the best results. Bulk ceramic that was too Tl rich did not produce uniform growth of superconducting phases on the wafer. Bulk ceramic that was Tl deficient produced good phase growth but with random orientation and very weak linked films. Furthermore, the bulk ceramics worked best if they were presintered for 20-40 minutes before being used to sinter films. The metal ratios in the as deposited films were very close to the desired $Tl_2Ca_2Ba_2Cu_3O_{10}$

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composition. Air sintering produces a slight weight gain due to oxidation and Tl uptake (<5 at. %). Although the films are typically superconducting after the air sinter process, subsequent oxygen anneals in some cases substantially improve the superconducting properties while not significantly affecting the morphology or stoichiometry [9]. Typical oxygen anneals were 10 min. (0.3 μm films) or 30 min (0.7 μm and thicker films) at 750 C followed by a furnace cool. The effects of oxygen annealing may be due to reduction of strain in the films, removal of cation disorder, or changes in the number of oxygen vacancies in the grains or at the grain boundaries.

The morphology composition and structure of the films were determined by scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDS) and by x-ray diffraction. The sintered films nucleate only at the substrate/film interface, and appear to produce highly oriented growth as evidenced by the planar morphology as seen by SEM. Although some epitaxial films have been produced, most of the films show complete c-axis orientation perpendicular to the substrate, but only partial a-axis orientation. These films are smooth on a submicron scale (± 0.1μm) and are highly dense (> 90%) with only isolated pinholes, for both 0.3 and 0.7 μm films. The grain size varies from 10 to >100 μm, the larger grains indicative of approaching true epitaxial growth. The film growth was quite reproducible as long as the bulk Tl ceramics were of the correct stoichiometry. Some films showed syntactic intergrowth where the $Tl_2Ca_2Ba_2Cu_3O_{10}$ and $Tl_2CaBa_2Cu_2O_8$ phases are intergrown. Films with intergrowths had superconducting properties as good as or better than those that were single phase.

While most of the films tested showed complete transitions resistively and magnetically, the transport properties were very sensitive to the sintering configuration and protocol. The sintered films with an air-only sinter had resistivities of 0.6 to 2 mΩ-cm, zero-resistance at 90 to 105 K and critical currents to 4.5 x 10^5 A/cm^2 at 76K. After oxygen anneals these films had resistivities of 0.5-1.6 mΩ-cm, zero-resistance from 104 to 109 K and critical currents to 6 x 10^5 A/cm^2. Films with high critical current densities show little or no drop in J_c with in-plane magnetic fields of up to 800 Oe, while poorer films (J_c below 10^5) show a substantial drop in J_c in these fields. Films with near optimum characteristics could be made quite reproducibly. Fig. 1 shows the resistivity versus temperature plot for a typical film. This film had a J_c of greater that 6 x 10^5 A/cm^2. Films with a room temperature resistivity below 1 mΩ-cm the films are not weak linked, and as discussed below, the critical currents appear to be dominated by flux flow effects. The lack of weak links in the best films is indicated by (1) the high J_c values; (2) the insensitivity of J_c to in-plane magnetic fields; and (3) large anisotropic demagnetization effects (>4500x) in the magnetic shielding at fields below H_{c1}.

On the other hand, it is clear that these films are not optimized for J_c because the flux pinning is very poor. This is illustrated by the magnetic hysteresis loops in Fig. 2 for a free surface air-only sintered 0.3 μm film on $SrTiO_3$. The hysteresis is very small above 0.3 T at 77 K, but is substantial to 0.5 T at 40 K. Loops at 5 and 20 K show that the hysteresis continues to increase with decreasing temperature. The dramatic decrease in hysteresis above 40 K shows easy flux motion and hence suggests weak flux pinning[12,17,18].

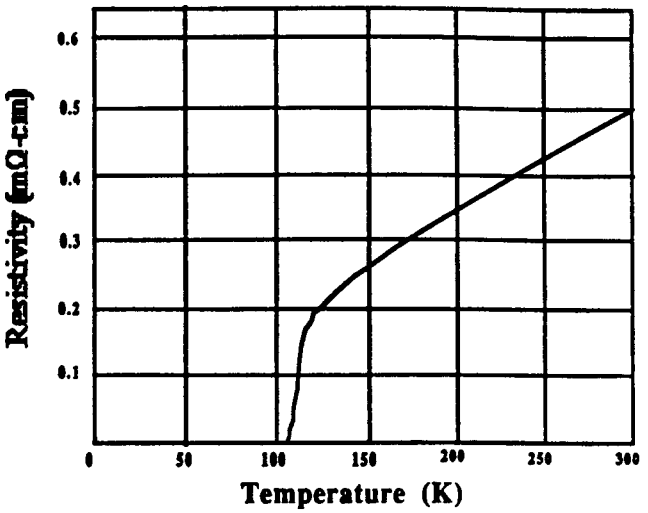

Figure. 1. Resistivity versus temperature for a $Tl_2Ca_2Ba_2Cu_3O_{10}$ c-axis oriented thin film on a $SrTiO_3$ substrate. The normal state resistivity of <0.5 μΩ-cm is indicative of no weak links. Zero resistance was obtained at 110K for the film and J_c was > than 6 x 10^5 A/cm^2.

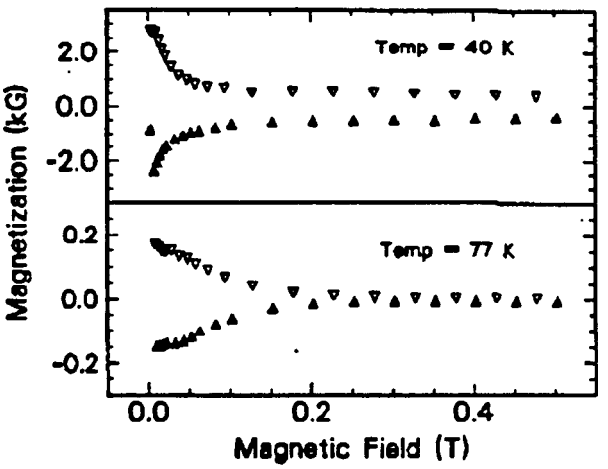

Figure. 2. Magnetization loops at 40 and 77 K with the field applied perpendicular to a 0.3 μm thick $Tl_2Ca_2Ba_2Cu_3O_{10}$ film on $SrTiO_3$. The solid triangles indicate increasing fields and the open triangles decreasing fields. The dramatic decrease in hysteresis with increasing temperature indicates activated flux motion (note the change in scale on the vertical axis) due to weak flux pinning.

Direct measurements of flux creep in these films confirm an activated component to the flux motion. For a 0.7 μm thick $Tl_2Ca_2Ba_2Cu_3O_{10}$ film on Y-ZrO_2 the data between 5 and 40 K yield an average flux pinning potential of 80 meV.[12] This earlier unoriented polycrystalline $Tl_2Ca_2Ba_2Cu_3O_{10}$ thin film showed an order of magnitude smaller transport critical current densities than our current films. However, flux creep measurements in 50 mT applied normal to the high quality epitaxial 0.3 μm-thick $Tl_2Ca_2Ba_2Cu_3O_{10}$ film used for the hysteresis data in Fig. 4 show a pinning potential of 56 meV, nearly the same as that for the poorer film. This result suggests that flux pinning is not a strong function of either film quality or thickness.

DISCLAIMER

Given such weak flux pinning, these films are not capable of achieving a true critical state defined by a uniform current density generating a Lorentz force which is just balanced by the pinning forces. Thus hysteresis loops such as those in Fig 2. are not true steady state measurements, and the inferred J_c values will be less than the measured transport value. To demonstrate the problems in applying the Bean critical state model [19] to a superconducting film with weak flux pinning, we can compare the inferred critical current densities J_{cm} from the magnetization hysteresis at 77 K with the direct transport values J_{ct}. The film used for the hysteresis study is an air only free surface sintered film of 0.3x0.3 cm^2 in area, and the remanent magnetization (low-field value following the loop at 77 K in Fig. 4.) is 175 G, yielding J_{cm} ~60x175/0.3 ~ 35,000 A/cm^2 compared to J_{ct} ~ 450,000 A/cm^2 at 76 K. The agreement between J_{cm} and J_{ct} is improved considerably at lower temperatures where the flux motion is limited. The remanent magnetization of 2.75 kG at 40 K (Fig. 4.) gives J_{cm} ~540,000 A/cm^2, and J_{cm} increases to $1.0x10^6$ A/cm^2 at 20 K and $1.5x10^6$ A/cm^2 at 5 K.

Device Basics

We can take advantage of the weak pinning in these films, and have made single-film devices that are based on parallel arrays of patterned weak links (narrow current paths in a ladder type arrangement) [20],[21]. As configured, the links operate in a flux flow regime. The links are not small enough to exhibit Josephson behavior but do exhibit interesting flux motion effects as expected from the weak pinning seen in the magnetization. The basic device, shown Fig. 3, has an array of links along with a control line that affects the device by generating a magnetic field. The distance across the links is about 5 μm and the bridge width is somewhat smaller. The original film thickness is typically around 300 nm and in the link region the thickness is reduced to between 50 and 100 nm with a controlled etch of dilute HNO_3.

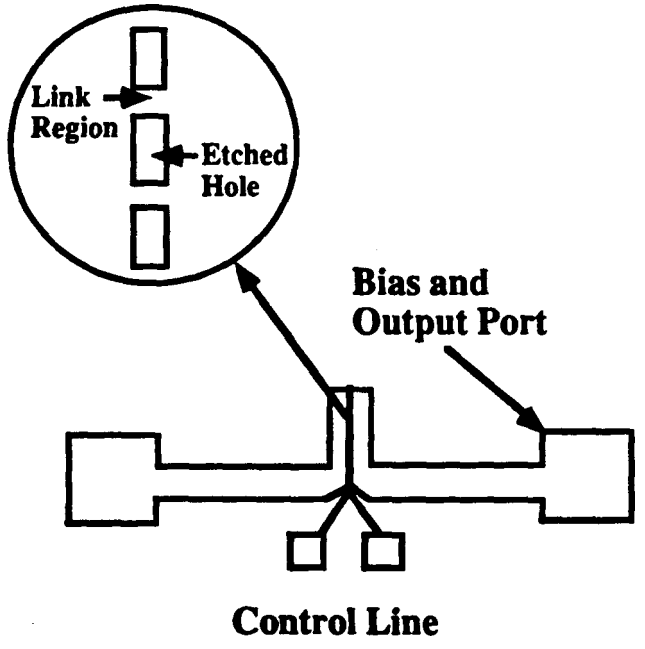

***Figure. 3** Schematic diagram of a single layer thin film HTS device employing an array of patterned weak links and a patterned control line.*

The basic mode of operation is to bias the device into a flux flow state and use the control line as a 'third terminal' to influence the device state. Some DC and RF experiments with this device are discussed below.

DC Characteristics

An IV curve is shown in Fig. 4a [22]. The zero voltage, flux flow and normal state regions are clearly delineated. As mentioned above, the flux flow region is of particular importance (evidence that it is flux flow will be presented below). In Fig. 4b the effect of control current on this region is illustrated. The effect can thus be modeled as a current controlled voltage source. The effect of the control current is measured by the transresistance which is the ratio of the terminal voltage change to the control current change. A typical transresistance for this device made of a single Tl film and operating at 77K is on the order of 10-15 Ohms.

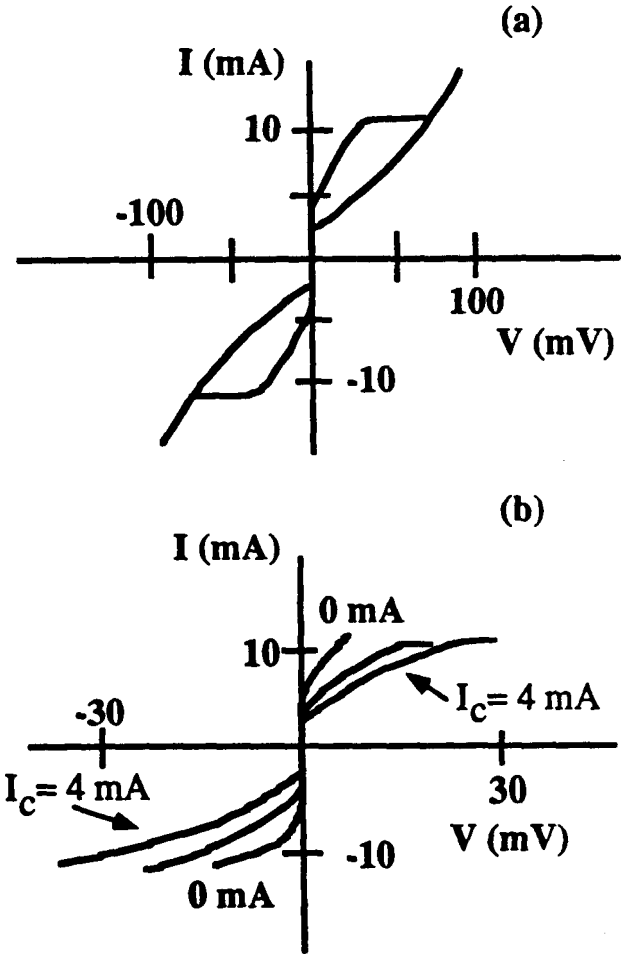

***Figure. 4** (a)I-V characteristics for a $Tl_2Ca_2Ba_2Cu_3O_{10}$ thin film device with the structure illustrated in Fig. 3. (b) I-V characteristics for the device in (a) but with a current (I_C) flowing in the control element.*

The existence of flux flow can be demonstrated with a variant of Giaever's DC transformer, as has been previously discussed [22]. One device is placed on top of another separated by a thin dielectric with the link regions of the devices aligned. A voltage was detected in the second device dependent on the bias in the first device. The electrical resistance between the two samples exceeded 20 megohms.

RF Characteristics

The first RF/microwave applications we investigated were linear circuits such as amplifiers. We have reported on S parameter measurements on these devices [23] and they do hold promise for some buffer amplifier applications if the transresistance can be increased.

Of more interest are nonlinear applications such as oscillators and mixers. We have reported on the former [24] where stable, narrow oscillations up to 12.6 GHz have been observed. We have also been studying mixer configurations and have observed mixing at frequencies over 35 GHz. A 35.7 GHz signal and a 35.71 GHz signal were applied to the device in a waveguide fixture and the terminal voltage of the device was monitored. The expected 10 MHz mixing product was observed without impedance matching or design optimization. This effect results from an inductance in the device body that is controlled (in value) by both the body current and the control current. The inductance varies quite linearly with control current so applications such as modulators are of interest. There are bias states in some applications where the inductance will vary non-linearly with body current. In this case the above applications as a mixer or an oscillator ar possible. The nonlinear applications seem particularly exciting and several are currently being investigated.

In summary we have found that the morphology and structure of superconducting thin films in the Tl-Ca-Ba-Cu-O system are controlled by the sintering process and can be tailored to be randomly oriented or highly oriented with the c-axis perpendicular to the substrate. The former is desirable for far IR detectors and rf SQUIDS while the latter is desirable for interconnects, rf and mm wave applications and other high current devices. The smoother morphology and higher density of the free surface sintered films are desirable for photolithographic patterning of these materials. The films grow in an oriented fashion between 0.3 and 0.7 μm thick. While oxygen annealing appears to be necessary to get high quality randomly oriented films, the oriented films show excellent properties after just an air anneal. We have also demonstrated a planar device that is particularly well suited to these materials and capitalizes on their weak flux pinning.

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