Thin film processing and device fabrication in the ^{OCT 12 1990}
Tl-Ca-Ba-Cu-O system

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ABSTRACT

An obvious group of applications for high temperature superconducting (HTS) materials is microwave and millimeter wave circuitry. Besides low loss, unique features of these materials, such as flux flow, can be exploited. We have been concentrating on the Tl-Ca-Ba-Cu-O family of materials. The film growth techniques, lithographic processing methods and characteristics of several devices we have developed will be presented. These devices include a flux flow-based transistor with demonstrated operation at frequencies above 35 GHz, real gain in a 50 Ω system and potentially useful non-linearities and impedance levels. A number of passive microwave components are under investigation to form a more complete HTS microwave technology group.

1. INTRODUCTION

Many microelectronic applications of HTS materials have been investigated to date ¹⁻⁴ including filters, detectors, modulators, etc.. In the pursuit of a more complete high frequency technology, a number of issues must be addressed. The film process must be stabilized and films with low surface resistance in the millimeter wave regime must be produced. Device processing technology must include lithography with resolution of better than a few μm , high quality contacts, and stable non-reactive deposition of dielectrics and normal metal layers compatible with the TlCaBaCuO film. Finally, active and passive device concepts must be found, that both fit the abilities of these unique materials and address applications requirements. The following represents the current state of such a technology development.

2. Tl-Ca-Ba-Cu-O FILMS2.1 Film growth

Due to the volatility of Tl, development of films in the Tl-Ca-Ba-Cu-O system has necessitated ex-situ processing. This processing consists of three main steps: deposition, sintering and annealing. Work to date indicates that the first step is not critical as long as an approximately correct stoichiometry is obtained and the formation of intermetallic phases is prevented. The second step, however, is crucial; phase and morphology are established during sintering in air. The third step, a controlled oxygen anneal, optimizes the superconducting properties of the films.

Metallic films are deposited by sequential electron beam evaporation of the pure metals onto the substrate of choice, which has been SrTiO₃ and LaAlO₃ (the latter used in the experiments described below), under a slight oxygen overpressure ($1-3 \times 10^{-5}$ mbar) to prevent intermetallic phase formation. The evaporations are done in layers starting with Cu and ending with Cu to encapsulate the structure. Film thicknesses of 0.3 μm , 0.7 μm and 1.5 μm have been made using 12, 25 and 49 total layers, respectively. Films as thin as 0.1 μm have been made using only layers of Cu, Ba, and Ca with Tl added during ex-situ processing. Layer thicknesses achieving stoichiometry for Tl₂Ca₂Ba₂Cu₃O_y (in

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the order deposited) are Cu: 159Å, Ba: 675Å, Ca: 450Å, and Tl: 298Å. The substrate temperature is kept below 50 °C. The as-deposited partially oxidized structures are metallic as expected and show no evidence of superconductivity. Such precursor films are sensitive to oxygen and moisture and consequently are stored in an argon atmosphere dry box while waiting to be sintered and annealed.

Precursor films are oxidized and the Tl-Ca-Ba-Cu-O superconducting phases synthesized during the sintering process. The morphology of the oxidized film is also established at this time. Liquid Tl phases, perhaps Tl₂O, appear to be crucial to the formation of clean, sharp grain boundaries. To date initial sintering in pure oxygen has not produced films with superconducting properties as good as for those films sintered in air and subsequently oxygen annealed, presumably because liquid phase formation is suppressed by sintering in oxygen.

Films are sintered with the substrate sitting face up on bulk Tl₂Ca₂Ba₂Cu₃O_y ceramic while a second bulk Tl₂Ca₂Ba₂Cu₃O_y ceramic is located above, but not in contact with the film. The "sandwich" structure is placed in a 3" Pt crucible with a tight fitting lid. The lid has an approximately 5 mm hole allowing Tl leakage and producing better quasi-equilibrium conditions of Tl and oxygen partial pressure. Films are sintered for 16 minutes at 850 °C. Primary device development has been done on films 0.3 μm thick.

The exact composition of the bulk ceramics used for the Tl source is critical. A narrow window of compositions from Tl_{2.04} to Tl_{1.96} produces the best results based on morphology, composition and superconducting properties. Bulk ceramics that are too Tl rich do not produce uniform growth of superconducting phases on the wafer, but tend to produce blocky localized growth with more voids. Bulk ceramics that are Tl deficient produce good Tl₂Ca₂Ba₂Cu₃O_y phase growth but with random orientation and weak links. Furthermore, the bulk ceramics work best if they are presintered for 20-40 minutes at 850 °C before being used to sinter films. The metal ratios in the films as deposited are very close (±5%) to the desired Tl₂Ca₂Ba₂Cu₃ composition. Sintering in air produces a slight weight gain due to oxidation and Tl uptake (<5 atomic %). Although the films are typically superconducting after sintering in air, subsequent oxygen anneals in some cases substantially improve the superconducting properties while not significantly affecting the morphology or stoichiometry. Typical anneals are 10 min. (0.3 μm films) at 750 °C followed by a furnace cool. In the best films the effect of this anneal is small with increases in T_c of 2-5 K and increases in J_c of ~10%. Poor films, however can be substantially improved with anneals as low as 400 °C and changes of 20 K in T_c and an order of magnitude in J_c have been observed. Possible effects of oxygen annealing include reduction of strain in the films, removal of cation disorder, and changes in the number of oxygen vacancies in the grains or at the grain boundaries.

2.2 Morphology and Structure

The morphology 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 0.3 μm films are smooth on a scale = 0.1 μm and are highly dense (> 90%) with only isolated pinholes. The grain size varies from 10 to >100 μm, indicative in some cases of an approach to true epitaxial growth. Cleaved films were examined by SEM normal to the substrate surface. In all cases the individual grain thickness is equal to the film thickness and no layering is observed. The lateral and vertical uniformity strongly supports the bulk superconducting nature of the films. 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 in the plane.

Although single phase films have been grown, with only sintering in air the films typically have greater proportions of the Tl₂Ca₂Ba₂Cu₃O₁₀ phase (~80%) than after a subsequent anneal in oxygen (~50%). The high degree of orientation observed indicates that the two phases are syntactically

intergrown. The $0.3\text{ }\mu\text{m}$ films before oxygen anneal show a slightly larger amount of the $\text{Ti}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$ phase relative to the $\text{Ti}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$.

3. PROCESSING DEVICES

All of the circuits to be described are made with standard optical lithography (using a solvent based negative photoresist) and wet etching. A solution of 2 % Br in isopropanol⁵ is used for mesa etching with an etch rate of approximately 30 nm/sec. With this process, stable $3\text{ }\mu\text{m}$ linewidths are obtainable. In some applications described below, controlled film thinning is required. For example, a narrow region (eg. $10\text{ }\mu\text{m}$ by $50\text{ }\mu\text{m}$) must have its thickness reduced from 300-700 nm to less than 100 nm. This is done with a carefully timed etch of 0.5-0.8% Br in isopropanol.

Dielectric and normal metal levels are also required in some applications. A hard-baked layer of negative photoresist works as an adequate dielectric for many applications (stable and low loss). Other dielectrics are under investigation. Most normal metals are, of course, usable for other layers. If the metal is in contact with a TiCaBaCuO level, it must not easily oxidize or oxygen may diffuse from the superconductor causing contact problems. Metals are currently used for such applications as resistors, normal metal control structures (used in one of the devices described below) and other purposes. The metals used are Au, Ti, Al, W-Si and Ag. The W-Si is used frequently as an oxygen diffusion barrier for Ti and Al resistors. For ohmic contacts, we use annealed silver contacts deposited through a shadow mask. Contact resistances of less than $0.2\text{ }\Omega$ have been achieved and do not appear to degrade with time.

4. DEVICES

The main device of interest to us so far has been called the Superconducting Flux Flow Transistor (SFFT)^{3,6,7,8}. It consists of a parallel array of weak superconducting links (separating two unweakened banks of superconductor) and a control line to provide a local magnetic field. An example of this structure is shown in Fig. 1. When the device is biased below the critical current (typically on the order of 1 mA), no flux is admitted into the link system (perfect Meissner state). Above the critical current, flux is admitted in discrete quanta known as vortices.⁹ These vortices can move since the bias current generates a Lorentz-type force on the vortices. This state of flux flow is used in device operation. The vortices are also subject to forces from external magnetic fields (from the control line), viscous damping, pinning forces (which are undesirable in that the average vortex speed is reduced) and surface barriers at the edges of the links which hamper flux entry and exit. The balance of these forces determines the flux motion and hence the terminal voltage. In terms of active device performance, the key principle is the use of an external magnetic field (via the control line) to modulate the flux density in the link system^{10,11} and the resulting flux motion.

Figure 1. A layout of the Superconducting flux flow transistor (SFFT). The links are about $5\text{ }\mu\text{m}$ by $10\text{ }\mu\text{m}$ and are about 100 nm thick (the banks are $300\text{--}700\text{ nm}$ thick). The control line provides a magnetic field that modulates the flux density in the link system.

A typical set of IV curves is shown in Fig. 2. The transition between the zero-voltage section and the flux flow section is apparent. By modulating the flux density in the link system, the control field causes a horizontal translation of the flux flow branches (with an accompanying change in critical current).

Figure 2. An IV curve set for the device of Fig. 1. Note the change from a zero voltage state to a flux flow state and the effects of control current I_c .

The device behavior is closely correlated to the quality of the film remaining in the link region. While a highly pinned material results in higher critical currents, it also reduces sensitivity to external magnetic fields (and hence gain) and reduces the flux speed and frequency response of the SFFT. A material with a low H_{c1} is desirable in that it is easier to admit flux to the system; this tends to increase sensitivity to the control fields. The penetration depth is also important since it strongly influences the surface barriers and hence control-field sensitivity¹². In addition, the effective penetration depth changes with link thickness, greatly increasing the effect of the film thinning process. Maximum gain occurs for links thinner than a penetration depth but not so thin that the superconductivity is destroyed or the defect density rises enough to induce excessive pinning centers. For a stable film production process, the effect of link thickness must be very reproducible (typical thickness of the active region is about 80 nm). Films with higher J_c tend to have narrower windows of acceptable link thickness but may still be used with good results. While not all possible material parameters have been considered here, the above group is a minimal set of important characteristics that must be considered when making the SFFT.

The next step in the development of microwave applications is the creation of an equivalent circuit. An equivalent circuit is shown in Fig. 3¹². The input impedance is low (a resistance of less than $1\ \Omega$ from contacts and surface resistance and an inductance of around 200-300 pH). This is a useful property when the SFFT is driven by a low impedance source (eg. a Josephson junction). For applications in a $50\ \Omega$ system, impedance matching is necessary. The output is dominated by the transresistance mechanism (a dual of the transconductance mechanism in a FET), an output resistance on the order of 3-5 Ω , and an output inductance that is non-linear. A transresistance (r_m) is used since a given point on the IV curve translates more or less horizontally with changes in control current. Transresistance is defined as the change in output voltage per unit change in control current. A typical value of r_m for a good TiCaBaCuO device at 7 K is 15-20 Ω . Both the transconductance and output resistance are constant for a wide range of biases. Hence the device has promise as a linear amplifier. The non-linearity of the output inductor is useful for applications such as phase modulation and phase shifting⁸.

Figure 3. An equivalent circuit for the device of Fig. 1. For large signal analysis, the output resistance is modeled as part of a non-linear voltage source. The output inductor can also have significant non-linearities.

Net device speed limits overall frequency response. Two factors affecting device speed are the input and output L/R time constants as can be seen from Fig. 3. By reducing device dimensions, these inductances can be reduced, in turn reducing the time constants below 50 ps in most circuits. Besides the circuit time constants, there is a fundamental device time constant as well. The vortices take a finite amount of time to cross the link system. This delay is the transit time constant. With vortex speeds on the order of 5×10^5 m/s (at 77K and no external field) and typical link dimensions (5 links, each 3 μ m in the direction of flux motion) this time constant is about 30 ps. As lithographic capabilities improve, this time constant can be reduced further. Device operation has been demonstrated at 35.8 GHz (a smaller device than that described above, used as a mixer) when the net time constant predicts a cut-off of 36.7 GHz¹². With higher resolution lithography and the use of millimeter-wave fixturing, operation in excess of 60 GHz seems feasible.

One promising feature of the SFFT is net gain in a 50 Ω system¹³. With some impedance matching, one group of devices have the gain shown in Fig. 4. While this is a resonant matched circuit, broader-band matching schemes are of course possible. The important point is that the available gain exceeds 20 dB. Because of the very low input impedance, very high gain can be achieved with perfect impedance matching. Preliminary noise measurements show a minimum noise figure of about 0.5 dB at 4 GHz¹⁴. Work continues on broader band amplifiers and on the evaluation of noise and non-linearities.

Figure 4. The lower picture is an SFFT embedded in its matching networks (composed of superconducting transmission lines). The upper picture shows the gain of this structure as a function of frequency. This very crude structure produced real gain over a bandwidth of about 0.7 GHz.

Another interesting application is that of an active impedance converter¹⁵. Since the input impedance is low, the SFFT can be easily driven by a LTS Josephson tunnel junction (in a high speed sampler for example). Josephson junctions have low output impedances (less than $1\ \Omega$) and low output voltage swings (on the order of 1 mV usually) so it is difficult to use them to drive conventional electronics directly. Since the output impedance of the SFFT ($> 5\ \Omega$) is larger than that of a tunnel junction and output signal swings of greater than 100 mV are available, the SFFT can much more easily drive an FET or other stage of conventional electronics. A circuit and the FET output response to a JJ switching event are shown in Fig. 5. The switching time for this circuit is about 100 ps and is fixture limited. With better fixturing, switch times of 50-60 ps should be possible, based on circuit and device time constants. This type of structure can be useful for connecting to existing Josephson based A/D converters or samplers.

Figure 5a The SFFT used as an active impedance converter between a low T_c Josephson junction (with low voltage levels and low impedances) and a GaAs MESFET. The voltage and impedance levels of the SFFT make it ideal for such an application. The junction bias is increased until the junction switches. The current through the SFFT control line then switches high causing a high voltage at the SFFT and the FET outputs.

Figure 5b. The time response of the FET drain voltage in the line driver configuration of Fig. 5a. The limiting time constant is that of the fixturing. The basic device time constant is on the order of 50 ps for this configuration.

Other applications of the SFFT are under investigation, but the SFFT is not the only device/circuit of interest. In particular, passive microwave circuits are also under development. Resonators, such as a ring structure, have been built and are useful for materials characterization¹⁶; a typical structure is shown in Fig. 6. An all-gold structure is first used to evaluate the surface resistance of gold. To evaluate the HTS material, other ring resonators were constructed using a TiCaBaCuO main conductor and a gold ground plane. With the gold surface resistance data and the data from the HTS resonator, it is possible to compute the TiCaBaCuO surface resistance. The method is valid for arbitrary film thicknesses and the structure is easy to measure using a contactless probe. While this structure does not have optimal sensitivity, it is relatively easy to characterize and the results are adequate for the vast majority of films presently available. For our films, we have measured a surface resistance of about $2 \text{ m}\Omega$ at 8 GHz and 77K. This can be compared to the theoretical value for gold of about $9 \text{ m}\Omega$ at 8 GHz and 77K. Coplanar waveguide filters and confocal resonators are also under investigation for applications and materials analysis respectively.

5. CONCLUSIONS

We have produced TiCaBaCuO films using e-beam evaporation with subsequent sintering and annealing that have critical current densities of at least several hundred kA/cm^2 , critical temperatures over 100K and surface resistance better than that of gold at 77K and 8 GHz. Processing techniques have been developed for making passive microwave elements and a four terminal active device called the superconducting flux flow transistor (SFFT) for microwave applications. The techniques include contacting, dielectric and normal metal layer deposition, and controlled HTS film etching. The SFFT shows promise as a microwave amplifier, oscillator and active impedance converter and may also have many other applications. The advantages of the device include high speed, potentially low noise and, for some applications, useful impedance levels. Passive resonators also show promise as demonstrated by us and many others.

Figure 6. The ring resonator and probe assembly to measure surface resistance in sensitive and relatively non-invasive manner. The fundamental resonant frequency of the structure shown is about 8.2 GHz.

6. ACKNOWLEDGEMENTS

Some of this work was performed at the University of Wisconsin-Madison, ECE Department. The authors wish to thank J. B. Beyer, J. E. Nordman and Gert Hohenwarter for assistance in the course of this research. This work was supported in part by a National Science Foundation Graduate fellowship, by the U.S. Department of Energy under contract No. DE-AC04-76P00789, and by DARPA, ONR and SDI under contract No. N0017390WR00172.

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