In situ pulsed laser deposition of superconducting $Ba_{1-x}K_xBiO_3$ thin films

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We have grown superconducting thin films of $Ba_{1-x}K_xBiO_3$ by *in situ* pulsed laser deposition from a stoichiometric ($x = 0.4$) target. The best films exhibit an onset transition temperature of 28 K and have zero resistance as high as 26 K. Films are single phase and highly oriented in the (100) or (110) direction on MgO, $SrTiO_3$, $LaAlO_3$, and Al_2O_3 substrates. We have observed high-quality normal-insulator-superconductor and superconductor-insulator-superconductor quasiparticle tunneling characteristics with the films.

Recent results have identified the cubic bismuthate $Ba_{1-x}K_xBiO_3$ (BKBO) as a potentially attractive material for superconductor electronic devices. For K concentration $x = 0.4$, BKBO has a bulk transition temperature of about 30 K, not as high as the high-temperature superconducting cuprates but considerably higher than the metals presently used in superconductor electronics (Nb and NbN). In contrast to the cuprates, BKBO has an isotropic structure and a moderately long coherence length (≈ 75 Å).[1,2] Most significantly, BKBO has exhibited excellent BCS-like quasiparticle tunneling characteristics in BKBO/Au junctions[3–5] and hysteretic Josephson tunneling behavior in BKBO/BKBO contacts.[6] These results have not been observed in the cuprates.

Thin films of BKBO and the related material Ba-Rb-Bi-O have been grown by sputtering[3] and by molecular beam epitaxy (MBE),[7] using a post-annealing procedure to attain high-quality films.[8] In this letter, we report the growth of BKBO films by an *in situ* pulsed laser deposition technique. Films are deposited from a superconducting stoichiometric ($x = 0.4$) BKBO target. We have successfully grown single-phase superconducting films on MgO, $SrTiO_3$, $LaAlO_3$, and Al_2O_3 using this approach.

Films are deposited using a standard pulsed laser deposition system that we have previously used to grow high-quality $YBa_2Cu_3O_{7-x}$ (YBCO) films. An ArF excimer laser (193 nm) is focused onto a pellet of BKBO with a fluence of about 0.5 J/cm^2 per pulse, about 1/3 of the power density we use for YBCO deposition. This fluence was chosen to give a plume height comparable to that used in our YBCO growth process. The target is a sintered and annealed powder pellet of $Ba_{0.6}K_{0.4}BiO_3$, the composition which has the maximum superconducting transition temperature in bulk samples.[2] The magnetic susceptibility of our target shows a sharp diamagnetic transition with an onset temperature at about 27 K.

The substrate is located on a resistive heater block 3–4 cm from the target face. Films are grown at a block temperature of 550–600 °C in pure Ar at a pressure of 1 Torr. With this laser fluence and substrate distance, we get a deposition rate of about 1 Å/pulse. Typically, we deposit at 4 Hz for 10 min, yielding a film growth rate of about 250 Å/min and a film thickness of 2500 Å. After deposition, we cool the film in Ar to 400 °C in about 10 min. At this temperature, we pump out the Ar gas, introduce O_2 at a pressure of 1 atm, and soak at 400 °C for 10 min. The film is then cooled to room temperature. No subsequent annealing is required. Longer anneals and external post-annealing have not improved film quality.

The deposition conditions chosen represent a trade-off between several factors. Measurements on bulk processed BKBO have pointed out the need to prepare the material in a reducing atmosphere to prevent the formation of stable K and Bi oxides that preclude growth of the superconducting BKBO phase.[2] There appears to be enough oxygen in the target itself to allow formation of the correct phase, and the film is fully oxygenated by adding a high pressure of O_2 during the cooldown. As a result, we deposit the film without ambient oxygen in a pure Ar environment, adding oxygen only when the sample temperature is below 400 °C. It is unlikely the Ar plays any direct role in the film nucleation and growth process, but we find that the background pressure stabilizes the laser plume. We also note that with this *in situ* procedure we do not observe as severe as microcracking as has been reported in MBE growth,[8] although cracking can be induced by growing very thick films (> 4000 Å).

The most critical parameter is the growth temperature. We find it is necessary to deposit at temperatures about 500 °C in order to form single crystalline phase BKBO; at lower temperatures (< 400 °C) we obtain amorphous films. The best structure is obtained for temperatures about 550 °C, but the volatility of K and Bi limits the maximum growth temperature to about 600 °C. Above this temperature, composition studies by Rutherford backscattering (RBS) indicate a deficiency of K. As a result, we have concentrated on films grown from 550 to 580 °C. Even for these films, we often find a slight deficiency of K and Bi compared to Ba by RBS, suggesting that the use of targets with excess K and Bi could improve the final film composition.

X-ray diffraction measurements indicate that the superconducting BKBO films have a single crystalline phase, with most exhibiting a mixture of (100) and (110) orientations. A typical θ-2θ scan is shown in Fig. 1 for a (100) $LaAlO_3$ substrate, showing strong (100) and weaker (110) reflections; we have expanded the higher order peaks to emphasize the absence of crystalline impu-

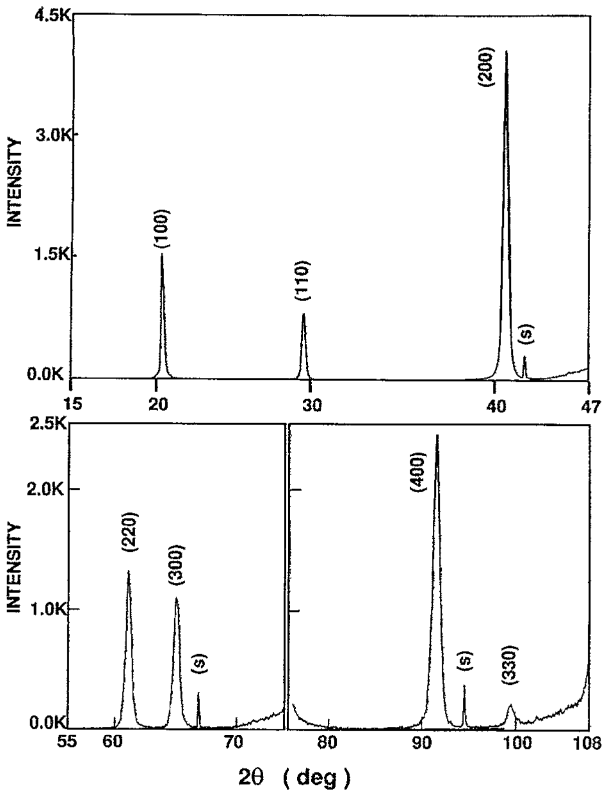

FIG. 1. X-ray diffraction θ-2θ scan using Cu $K\alpha$ radiation ($\lambda = 1.541$ Å) for a typical BKBO film grown on a (100) $LaAlO_3$ substrate. The film exhibits a single crystalline phase with a mixture of predominantly (100) and some (110) orientation. We have expanded the trace at large angles to demonstrate the absence of crystalline impurity phases.

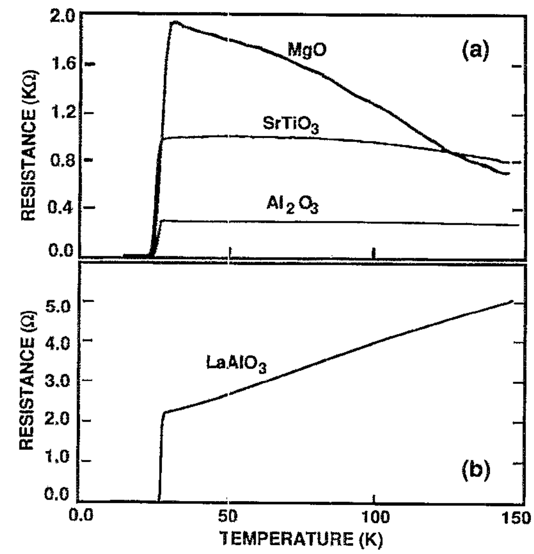

FIG. 2. Resistance vs temperature for several BKBO films exhibiting (a) semiconducting and (b) metallic behavior in the normal state. All measurements are taken with roughly the same film thickness and contact geometry for which 200 Ω corresponds to a resistivity of about 1 mΩ cm. The substrate material for each film is indicated to show the variety of substrates used; we do not necessarily intend to imply that these results indicate the relative merits of the materials. Note the much lower resistance of the metallic films for comparable measurement geometries.

rity phases. We have also grown essentially pure (100) films on (100) perovskite substrates, and completely pure (110) oriented material on (110) $SrTiO_3$ substrates. The cubic lattice constant is always in the range 4.28–4.30 Å, in agreement with the bulk value for films with the optimum superconducting properties.

Electrical resistance versus temperature data for BKBO films grown on several different substrates are plotted in Figs. 2 and 3. Most of our films have been deposited on (100) oriented $LaAlO_3$ and MgO substrates, but we have also successfully grown superconducting films on (100) and (110) $SrTiO_3$, and on $(1\bar{1}02)$ Al_2O_3. In most films, we observe semiconducting behavior in the normal state as shown in Fig. 2(a). For some samples, the resistance increases by up to a factor of 10 as the film is cooled from room temperature to 30 K; more often the increase is by less than a factor of 2 and the resistance is relatively flat or slightly decreasing near the transition. From the film thickness and contact geometry, we estimate the resistivity at the onset of the superconducting transition for these semiconducting films to be 1–10 mΩ cm. However, we have also fabricated films that exhibit purely metallic behavior as in Fig. 2(b). The film shown was grown on (100) $LaAlO_3$, and exhibits a nearly linear temperature variation from room temperature to its transition. This behavior is also characteristic of the cuprate superconductors, especially the 123 materials, and its origin remains a mystery. The resistivity at the transition for the metallic films is considerably lower, less than 100 $\mu\Omega$ cm. This result strongly suggests that the semiconducting behavior observed in the other film is not intrinsic to the BKBO but arises from intergrain material; this material is probably amorphous since we detect no other crystalline phases by x-ray diffraction. The metallic films also exhibit a considerably sharper transition as compared to the semiconducting films, as demonstrated in Fig. 3. The best film has an onset at 28 K and zero resistance at 26.5 K. Most films exhibit a lower temperature onset ($\approx$26 K) and a broader transition, reaching zero resistance by 22–23 K. On Al_2O_3, we observe a long resistive tail and have achieved zero resistance only at 20 K.

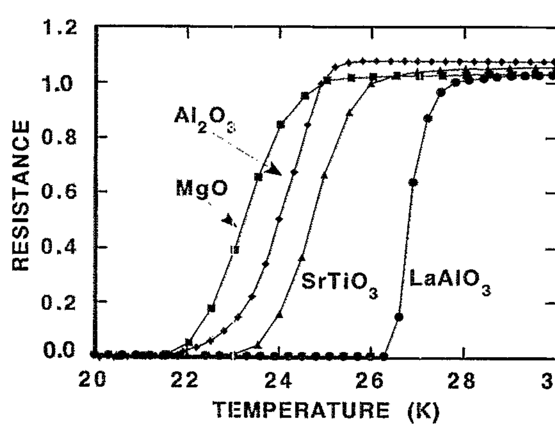

FIG. 3. Resistance vs temperature near the superconducting transition for the same BKBO films shown in Fig. 2. Film resistances are normalized to comparable values at 30 K to emphasize the shape of the transitions.

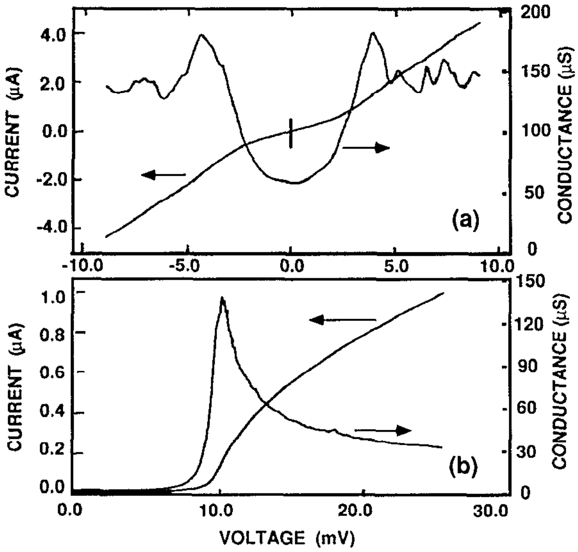

FIG. 4. Current-voltage curves and the differential conductance for (a) BKBO film/Ag paint contacts, and (b) two BKBO films pressed together, showing BCS-like NIS and SIS tunneling characteristics.

We have also measured the zero-field-cooled magnetic susceptibility of the films using an rf superconducting quantum interference device (SQUID) susceptometer. The films show a diamagnetic signal with an onset of 24–27 K. The film susceptibility transition is broadened compared to the response of the ablation target.

The most interesting and important property of the BKBO films is their ability to form tunnel junctions. We almost always observe normal-insulator-superconductor (NIS) tunneling characteristics between the films and Ag paint pads used for electrical contact; the barrier is most likely a native surface oxide. An example is shown in Fig. 4(a); the dynamic conductance is plotted on the same graph. Nearly ideal BCS curves have been obtained on these films by point contact tunneling.[9] The energy gap is consistently about 4.5 meV, giving a value of $2\Delta/k_BT_c$ of 3.8–4.0. This is in good agreement with strong-coupling BCS theory and with previous tunneling data on films and crystals.[4,5] We have also succeeded in making superconductor-insulator-superconductor (SIS) tunnel junctions by pressing two BKBO films together. The current-voltage curve, shown in Fig. 4(b), exhibits extremely low subgap conductance and a sharp rise at $2\Delta = 9$ meV. A Josephson supercurrent could not be detected due to the high junction resistance. Electronic devices based on this material should be operable at frequencies well above 1 THz, ideal for high-frequency circuits and submillimeter detectors. Realization of this technology will require fabrication of multilayer devices and studies of the high-frequency response and losses of BKBO films.

In summary, we have fabricated superconducting BKBO thin films on a variety of substrates by *in situ* pulsed laser deposition. The films exhibit onset of superconductivity at 28 K and achieve zero electrical resistance at temperatures up to 26 K. We see a linear resistivity with temperature in the best films reminiscent of other high-temperature superconductor films, but tunneling results suggest that BKBO behaves as a conventional BCS superconductor. We have obtained SIS tunneling curves that are promising for high-frequency quasiparticle detectors and superconducting electronics.

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