Epitaxial Cuprate Superconductor/Ferroelectric Heterostructures

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Thin-film heterostructures of $Bi_4Ti_3O_{12}/Bi_2Sr_2CuO_{6+x}$ have been grown on single crystals of $SrTiO_3$, $LaAlO_3$, and $MgAl_2O_4$ by pulsed laser deposition. X-ray diffraction studies show the presence of *c*-axis orientation only; Rutherford backscattering experiments show the composition to be close to the nominal stoichiometry. The films are ferroelectric and exhibit a symmetric hysteresis loop. The remanent polarization was 1.0 microcoulomb per square centimeter, and the coercive field was 2.0×10^5 volts per centimeter. Similar results were obtained with $YBa_2Cu_3O_{7-x}$ and $Bi_2Sr_2CaCu_2O_{8+x}$ and single-crystal $Bi_2Sr_2CuO_{6+x}$ as the bottom electrodes. These films look promising for use as novel, lattice-matched, epitaxial ferroelectric film/ electrode heterostructures in nonvolatile memory applications.

HE RECENT SUCCESSES IN THE growth of high-quality single crystalline thin films of the high-temperature cuprate superconductors have spurred interest in other similar perovskite materials with a variety of physical properties. Prime among these materials are the ferroelectric perovskites. Ferroelectrics have shown great promise in digital memory systems for both dynamic and permanent data storage (1). However, unlike their magnetic counterparts, they have not found their way into the multibillion computer memory market for a variety of reasons. One reason was that earlier researchers used large single crystals or thick (of the order of micrometers) films, both of which require large applied voltages (of the order of a few hundred volts) to reverse the polarization. These large applied voltages were incompatible with that used in semiconductor-based integrated circuits, which is generally 5 V. Another reason was that the films were generally polycrystalline and suffered from drawbacks such as aging, fatigue, and so on. We are trying to address all or many of these problems by creating lattice- and chemistry-matched heterostructures of the ferroelectric perovskites with the cuprate superconductors to yield single crystalline films. The metallic properties of the superconducting cuprates are utilized in the bottom electrode. Both the chemistries and the crystal lattices of the perovskite ferroelectrics are similar to those of the cuprate superconductors. The main difference between the existing technology for ferroelectric random access memories (FRAMS) and the proposed epitaxial heterostructure technology is illustrated in Fig. 1, A and B. In the currently used structure (Fig. 1A), the bottom electrode, which is typically Pt or Al, is grown as a polycrystalline layer on top of a substrate such as Si. The ferroelectric film is then grown on top of the electrode. Because the electrode is neither epitaxial nor single crystalline, the perovskite ferroelectric film is not single crystalline. The polycrystalline microstructure of the ferroelectric film has important consequences for the film



Fig. 1. (A) Schematic illustration of the current method for the deposition of ferroelectric thin films onto Pt-coated substrates. (B) Schematic of the new epitaxial oxide superconductor electrode/ ferroelectric heterostructure grown in situ by pulsed laser deposition.

properties: (i) the grain boundaries in it are sites for charge segregation and subsequent charge decay and (ii) these structural interfaces are also sites for chemical segregation or the formation of secondary phases, which are detrimental to film performance. For example, several of the critical properties of technological relevance, such as fatigue, aging, time-dependent decay of the polarization, and leakage current, are likely to be direct consequences of the polycrystalline microstructure. The details of these processes are discussed in recent review articles (1-3).

In the structure we have fabricated (Fig. 1B), the bottom electrode can be any of the high-temperature superconducting perovskite oxides. Typically, we use YBa₂Cu₃O_{7-x}, the "2201" and "2212" phases in the Bi-Sr-Ca-Cu-O system. These perovskite-based compounds grow epitaxially, with the *c*-axis normal to the substrate surface, on the [100] surface of single crystalline perovskite or cubic substrates such as SrTiO₃, LaAlO₃, MgAl₂O₄, and so forth. The ferroelectric film, typically bismuth titanate, barium titanate, or lead zirconatelead titanate, is then grown epitaxially on the superconducting oxide. Earlier work has shown that bismuth titanate is suitable for memory and electro-optic switching applications (4-7). After the ferroelectric film has grown, the top electrode, which can be either gold or another layer of the superconducting oxide, is grown. The structural quality of the top electrode is not as critical as that of the bottom electrode. This report presents results on the growth and characterization of such epitaxial heterostructures, specifically those in which the metallic layer was the Bi2Sr2CuO6+x superconductor and the ferroelectric film was Bi₄Ti₃O₁₂.

The heterostructures are grown in situ by pulsed excimer laser ablation. A 248-nm KrF excimer laser is directed at a rotating, sintered polycrystalline target of the required material, and the resulting plume is caught on a heated substrate. The targets are mounted on a four-target rotating carousel, thus enabling in situ deposition of the multilayered structure. The substrate heater is maintained at a temperature in the range of 650° to 820°C. The substrate surface temperature is about 50°C lower than the substrate heater temperature. The deposition is carried out in an oxygen pressure of 50 to 200 mtorr, and the films are grown at the rate of 0.5 to 1.0 Å s^{-1} .

Before growing the heterostructure, we determined the optimum conditions for the individual layers by deposition onto [100] SrTiO₃ substrates. At this stage, the quality of the film was determined by means of x-ray diffraction rocking curve measure-

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Fig. 2. An x-ray diffraction pattern from a $Bi_2Sr_2CuO_{6+a'}/Bi_4Ti_3O_{12}/SrTiO_3$ heterostructure showing the existence of sharp diffraction peaks from the 001 lines of the two layers and the substrate.

ments and Rutherford backscattering (RBS) channeling yields. The metallic nature of the bottom electrode was confirmed from the positive slope of the resistivity-temperature plot of single-layer films deposited under identical conditions. The following is a typical example of the heterostructure growth. The $Bi_2Sr_2CuO_{6+x}$ layer was grown at a substrate heater temperature of 740°C to a thickness in the range of 1000 to 2500 Å. The heater temperature was then changed to the optimum value for the Bi₄Ti₃O₁₂ layer, which was deposited to a thickness in the range of 1000 Å to 1 µm. We structurally characterized the multilayers using x-ray diffraction, RBS channeling, and planar section transmission electron microscopy. We characterized their electrical properties using a standard Sawyer-Tower circuit (8) in the frequency range of 1 Hz to 1 MHz.

We recorded x-ray diffraction patterns from a SrTiO₃/Bi₂Sr₂CuO_{6+x}/Bi₄Ti₃O₁₂ heterostructure in which both layers were deposited at a substrate heater temperature of 740°C (Fig. 2). All of the diffraction peaks observed, including those from the substrate, can be indexed as the 001 lines from Bi₄Ti₃O₁₂ or from Bi₂Sr₂CuO_{6+x}. The absence of diffraction peaks other than the 001 lines indicates that both layers are c-axis-oriented. Rocking curves about the 006 line of Bi₄Ti₃O₁₂ and the 008 line of the 2201 phase yielded a full width at half maximum of 0.7° to 1.0° for both peaks, indicating a large density of structural defects in the layers. The crystallographic unit cell in both the layers has glide planes (9, 10); hence, shear defects are easy to introduce. These types of defects can increase the rocking angle.

RBS studies were carried out in a random orientation to determine the stoichiometry of the films. The films were also examined along the [001] direction to determine the channeling yield, which is a measure of the crystalline quality of the film. An RBS spectrum from the heterostructure in the random orientation revealed the composition of the two layers to be close to the nominal values. The channeled spectrum showed a minimum yield at the surface of about 27%, indicating the presence of stacking defects in the layered structure.

Transmission electron microscopy (TEM) studies confirmed the epitaxy between the two layers and the substrate (Fig. 3). This TEM image of a cross section shows the substrate, the bottom 2201 electrode layer, and part of the $Bi_4Ti_3O_{12}$ layer on top. The selected area diffraction pattern shown in the inset reveals the epitaxial relation between the two layers and the SrTiO₃ substrate. A considerable density of structural defects can be observed in the $Bi_4Ti_3O_{12}$ layer (which was predicted by the RBS channeling studies), although the bottom electrode layer was relatively free of defects.

The electrical properties of the ferroelectric film were examined with a simple Sawyer-Tower circuit. We evaporated 200 μ m \times 200 µm Ti-Au pads onto the surface of the heterostructure to form the top electrode. The bottom electrode was contacted from the edge of the sample with Ag paint. The films exhibit ferroelectric hysteresis, as illustrated in Fig. 4. The remanent polarization is $1 \ \mu C/cm^2$ at a frequency of 1 kHz, which compares to 4 μ C/cm² for a single crystal in the same orientation. The coercivity is about 200 kV/cm, which is much higher than that obtained in single crystals (50 to 70 kV/cm) and bulk samples. The smaller remanence is probably due to the thickness of the films (about 2000 Å) or may be inherent to epitaxial films. The



Fig. 3. Cross section transmission electron micrograph Bi₂Sr₂CuO_{6+x} of the Bi₄Ti₃O₁₂/SrTiO₃ heterostructure. Large arrows indicate phase interfaces and small arrows show isolated stack defects in Bi2Sr2CuO6+x. The inset shows a selected area diffraction pattern, which confirms the epitaxy between the The lower three layers. $Bi_2Sr_2CuO_{6+x}$ layer is less defective in comparison to the upper Bi₄Ti₃O₁₂ layer.



Fig. 4. A polarization–electric field plot for the sample in Fig. 3, illustrating the existence of ferroelectric hysteresis with a remanent polarization of $1.0 \,\mu$ C/cm² and a coercivity of 200 kV/cm. The lower remanence (as compared to single crystals) is likely due to either the thickness of the film (about 2500 Å) or incomplete saturation.

larger coercivity is probably due to the large density of structural defects that assist in domain wall pinning. Thicker films have yielded a larger value of remanent polarization. The dielectric constants of the films are in the range of 130 to 180, and a loss tangent of about 2% has been obtained in the best heterostructures. Similar properties have been obtained with $YBa_2Cu_3O_{7-x}$ and $Bi_2Sr_2CaCu_2O_{8+x}$ as the bottom electrode layers.

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Calcic Micas in the Allende Meteorite: Evidence for Hydration Reactions in the Early Solar Nebula

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Two calcic micas, clintonite and margarite, have been identified in alteration products in a calcium- and aluminum-rich inclusion (CAI) in the Allende meteorite. Clintonite replaces grossular in alteration veins, and margarite occurs as lamellae in anorthite. Their occurrence suggests that, in addition to undergoing high-temperature alteration by a volatile and iron-rich vapor that produced the grossular and anorthite, some CAIs underwent alteration at moderate temperatures (\leq 400 kelvin). Petrographic evidence suggests that the calcic micas formed before accretion but after the formation of the layered rim sequences that surround the CAI. These calcic micas provide strong evidence that, contrary to theoretical calculations, some hydration reactions occurred in the early solar nebula.

A- AND AL-RICH INCLUSIONS (CAIS) are refractory objects that formed at high temperatures in the early solar nebula (1) and are prominent in the Allende CV3 carbonaceous chondrite. Many CAIs, however, contain features such as veins and complex rims that suggest extensive alteration by vapor or aqueous fluids (2-6). All CAIs in Allende have apparently undergone some alteration that has primarily affected melilite (4). Of particular interest among the alteration products are the phyllosilicates. The coexistence of low-temperature hydrated phases with highly refractory minerals poses intriguing questions regarding the thermal evolution of CAIs, the conditions for the formation of hydrous phases, the processes involved, and the relative timing of the alteration event or events.

We studied the alteration features in a coarse-grained CAI from Allende, using scanning electron microscopy (SEM), highresolution transmission electron microscopy (HRTEM), and analytical electron microscopy (7). Earlier TEM studies identified several phases in alteration products in Allende CAIs (8). However, those observations were from mineral separates; therefore, textural relations among phases were lost. We studied ion-thinned samples in which textures and intergrowths are preserved and identified two calcic micas, clintonite [ideally Ca(Mg,Al)₃(Al₃Si)O₁₀-(OH)₂] and margarite [ideally CaAl₂(Al₂- $Si_2OO_{10}(OH)_2$]. The occurrence of these minerals allows constraints to be placed on the thermal history of CAIs and on reactions in the early solar nebula.

Clintonite and margarite are the trioctahedral and dioctahedral members, respectively, of the calcic brittle mica group. Clintonite is rare in terrestrial rocks; it typically occurs in calc-silicate rocks that have undergone extensive metasomatism (9-11). Experimental studies of phase equilibria and of fluid compositions from natural mineral assemblages suggest that water-rich fluids and appropriate bulk compositions are required for the formation of clintonite (1113). Margarite is common in low- to medium-grade metamorphic rocks (14); its stability and compatibility relations are well constrained by experimental phase equilibria studies (15-17).

The CAI we studied is a type-A inclusion, with an interior composed of coarse-grained gehlenite $(Ca_2Al_2SiO_7)$ and minor fassaitic clinopyroxene. The gehlenite grains (80 to 90% gehlenite component) contain kink bands. Spinel, perovskite, hibonite, and FeNi metal occur as inclusions in the silicates. Opaque assemblages (fremdlinge) of FeNi metal, iron sulfides, calcium phosphates, V-rich spinels, and other phases occur in large (up to 300 µm) aggregates. The CAI is surrounded by a poorly developed Wark-Lovering (W-L) rim sequence that is 100 µm wide. W-L rims are believed to have formed during a rapid heating event that vaporized material from the surfaces of CAIs, leaving behind a refractory residue (2).

Millimeter-sized laths of gehlenite in the interior of the inclusion show the effects of alteration along cracks, cleavage planes, and grain boundaries. The veins of alteration extend from the surface of the inclusion, through the W-L rim, and into the interior. Grossular (Ca₃Al₂Si₃O₁₂), anorthite (CaAl₂-Si₂O₈), clintonite, and an unidentified, finegrained Na-Mg-Ca-Fe-Al-silicate occur in the altered areas. Relict grains of gehlenite with a high density of crystal defects also occur in the veins. Polysynthetic twinning in the gehlenite is common and increases toward the rim of the CAI. Polysynthetic twinning has been observed in metamorphic but not in igneous gehlenite (18).

Clintonite partially replaces grossular in one of the alteration veins in gehlenite. Individual clintonite crystals are 10 to 40 nm wide parallel to the c axis, are 100 to 500 nm long, and occur in pods up to 600 nm in diameter (Fig. 1). Energy-dispersive x-ray spectrocopy



Fig. 1. Low-magnification TEM image of a clintonite (Cn) pod surrounded by grains of grossular (Gr).

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