Transmission Electron Study of Heteroepitaxial Growth in the BiSrCaCuO System

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Abstract

Films of $Bi_2Sr_2CaCu_2O_8$ and $Bi_2Sr_2CuO_6$ have been grown using Atomic-Layer-by-Layer Molecular Beam Epitaxy (ALL-MBE) on lattice-matched substrates. These materials have been combined with layers of closely-related metastable compounds like $Bi_2Sr_2Ca_7Cu_8O_{20}$ (2278) and rare-earth-doped compounds like $Bi_2Sr_2Dy_xCa_{1-x}Cu_2O_8$ (Dy:2212) to form heterostructures with unique superconducting properties, including superconductor/insulator multilayers and tunnel junctions. Transmission electron microscopy (TEM) has been used to study the morphology and microstructure of these heterostructures. These TEM studies shed light on the physical properties of the films, and give insight into the growth mode of highly anisotropic solids like $Bi_2Sr_2CaCu_2O_8$.

I. INTRODUCTION

$Bi_2Sr_2CaCu_2O_8$, called 2212, is the prototypical compound of a class of layered copper-oxide superconductors which have been studied extensively due to their high superconducting critical temperatures T_c. Other known compounds in the BiSrCaCuO family, with the general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, include $Bi_2Sr_2CuO_6$, called 2201, and Bi_2Sr_2Ca2Cu3O10, called 2223. Like other cuprate superconductors, 2212 is a highly anisotropic layered compound, with lattice parameters a = 3.818Åand c = 30.66Å.[1,2] Despite the complexity of the large unit cell, layer-by-layer growth of films has been achieved, as has been demonstrated by the observation of oscillations in the intensity of reflection high-energy electron diffraction (RHEED) features during deposition.[3] Many cubic materials, notably GaAs, Si and various transition metals, can also be grown in a layer-by-layer fashion, so in itself the occurrence of RHEED oscillations is not remarkable. The unusual aspect of the 2212 oscillations is that each molecular unit is composed of 14 layers so that the cyclical growth pattern involves the formation of ordered layers within the unit cell as well as the accumulation of completed unit cells. Putting 2212 films in a multilayer along with other BiSrCaCuO compounds adds a further level of complexity. Because of the three different levels of ordering and the intrinsically strong anisotropy, the dynamics of growth in a multilayer made up of 2212 and its analogs can therefore be expected to be quite different from the case of semiconductor or metallic multilayers.

Cross-sectional TEM is a useful tool for studying the microstructure of multilayers and for classifying stacking faults in layered structures. Here TEM images have been used to study the morphology of single films and heterostructures of BiSrCaCuO compounds which have been grown using ALL-MBE. This is a recently developed technique involving sequential deposition of materials from metal vapor sources (thermal effusion cells) in a highly reactive ozone atmosphere.[4] The ALL-MBE technique has made possible growth of high-quality multilayers and thereby fabrication of Josephson junctions with novel tunnel barriers.[4–6] Described below are TEM observations of a sampling of the heterostructures which can be grown by ALL-MBE, including 2212/2201 multilayers and heterostructures with 2278 barrier layers. In addition, the occurence of planar and line defects in 2212 and 2201 will be described and discussed in relation to the unusual growth modes of these materials. The TEM micrographs will be interpreted in comparison to image simulations produced by a sophisticated electron-ray-tracing software package.

II. EXPERIMENTAL

The films used in this study were all grown using the ALL-MBE technique, which has been described in detail previously.[5] ALL-MBE is a variant of molecular beam epitaxy in which the composition and structure of a growing layered film are controlled by sequential evaporation of the constituent metals and their oxidation. The growth is performed in a highly reactive ozone atmosphere at elevated temperatures between 650 and 700°C. Growth is monitored in situ by observing reflection high-energy electron diffraction patterns, and post-growth characterization has been performed by x-ray diffraction, Rutherford backscattering (RBS), Auger electron spectroscopy (AES), x-ray fluorescence (XRF), secondary ion mass spectroscopy (SIMS), and atomic force microscopy (AFM). The RHEED observations confirm that abrupt changes in crystalline phase can be made, namely that ALL-MBE allows alternate layers of 2212 and 2201 to be grown as a superlattice.[4] RBS, AES and EDAX measurements confirm that the stoichiometry of the films is within a few percent of the nominal value.[7] X-ray diffraction measurements show that single-phase growth is possible using the ALL-MBE technique.[8] Total film thickness is typically on the order of 1000 Å. The superconducting transitions of all films used for TEM studies were measured resistively and found to be narrow, with a transition temperature T_c similar to that reported earlier.[6] Films like those used for TEM sample preparation have been fabricated into tunnel junction devices.[5]

Preparation of high-temperature superconducting films for examination by TEM has proven to be difficult. The major difficulties are as follows: differential thinning rates between substrate, film materials and materials used to fabricate the cross-section specimen; the inherent brittle nature of substrate and film materials; and the production of specimen-preparation-induced artifacts such as ion damage and amorphization. The results of these problems are specimens with only a small transparent region, fracture of the substrate and delamination of the film. To reduce and avoid the occurrence of these specimen preparation difficulties, advanced techniques are employed. The specimen preparation procedure described here employs a number of steps to avoid mechanical damage and reduce artifacts.

The basic construction of the cross-sectioned specimen is similar to the techniques describe by Newcomb[9] and Bravman.[10] The following is a detailed description of how their procedure has been adapted for BiSrCaCuO films.

To begin with, a piece of blank Si wafer is epoxied to the $SrTiO_3$ substrate of the superconducting thin film. The long direction of the Si strip is oriented on the surface of the film-substrate combination along the predetermined TEM viewing direction; i.e., [010] or [110]. The substrate is then trimmed away with a low speed diamond saw. The remaining Si/epoxy/film/substrate composite is laminated with epoxy between two semi-circular brass rods and inserted into a brass tube filled with epoxy. After curing, discs measuring .5 mm thick are sliced from the brass rod using a low-speed diamond saw. Disc specimens are lapped using a gravity feed holder from one side using a succession of fine diamond lapping films to a thickness of .25 mm. The specimen disc is then final polished on a vibrating polishing machine for several hours. Prior to lapping the second side, a Cu grid is epoxied to the polished surface for support. The second side is then lapped using the same diamond grit films to a final specimen thickness of 100 μm (excluding the Cu grid). The specimen is dimpled from the second polished side directly on top of the Si/$SrTiO_3$ interface. The dimpling conditions are: 15 g load, 60 rpm, 2-4 μm diamond powders. The final dimpled specimen thickness prior to ion milling is approximately 15-20 μm. Dimpling to thinner dimensions often caused the substrate to fracture or the film to delaminate. Then a Gatan, Inc. PIPS ion mill is used to sputter the film at a low angle of 4.5°. Low-angle ion milling in combination with ion beam modulation is utilized to reduce the difference in ion milling rates between the substrate, film, epoxy and Si. The first side of the specimen (dimpled side) is ion milled for about 90 min. The specimen is turned over and ion milled until perforation. After perforation both sides are again low-angle ion-milled at 1.5 keV to reduce surface damage. The specimen is examined using low-resolution electron microscopy, and if necessary is returned for further ion milling.

In order to characterize the layering and defect microstructure of these atomically engineered films, high resolution electron microscopy (HREM) was utilized. A top entry JEOL 4000EX with a point-to-point resolution of 0.17 nm was used to image atomic structure detail in cross-sectioned specimens having film orientations of [010] and [110]. Experimental images were recorded near the scherzer defocus value ($\approx$ -45 nm) and the first cross-over of the contrast transfer function ($\approx$ -75 nm). Images were also recorded at other defocus values at which specific layering and atomic structure detail was best resolved. The instrumental imaging conditions were as follows: 400 keV accelerating voltage, $C_s = 1.0$ mm, focus spread $\approx$8.0 nm, beam semi-divergence angle $\approx$0.8 mr and an objective aperture radius of 0.096 nm^{-1}.

The atomic structure of the layering was confirmed by comparison of the experimental images to those of simulated images. Calculation of the simulated images was performed using the MacTemPas software package.[11] Published lattice constants were used as inputs for 2201 and 2212, while lattice constants for 2278 and 1278 were estimated by using the same interatomic spacings as in the equilibrium phases. Since the specimen thickness and defocus conditions are unknown for particular images, calculations were performed for a range of values of these parameters.

III. RESULTS

A. 2212 overgrowth on $SrTiO_3$

Figure 1 shows a high-resolution image of 2212 overgrowth on a $SrTiO_3$ (001) substrate surface. $SrTiO_3$ has a lattice constant of 3.936 Å, while that of 2212 in the c-axis direction is 30.7Å.[1,2] Examination of the image shows that the ratio of the interplanar spacing in the $SrTiO_3$ to that in the epilayer is in rough agreement with the ratio of the lattice constants. In addition, one can see good continuity between planes of atoms in the $SrTiO_3$ and in the overlayer, indicating a coherent interface.

The most remarkable feature of the image shown in Figure 1 is the lack of conformity of the 2212 film to substrate surface features. In the center of the image, there is an asperity on the surface of the substrate. The bright lines in the 2212 film are thought because of the image simulations (discussed further below) to be BiO planes. In the immediate vicinity of the defect, there is a slight amount of disorder in the BiO planes, but this disorder is healed on a very short lateral scale beyond which the BiO planes are straight and unbroken. In the vertical direction, the BiO planes are continuous at only two 2212 molecular layers above the substrate. Somehow the 2212 layer is able to accomodate the distortion caused by the substrate roughness within a single unit cell. The result is that after only two monolayers of 2212 growth, the surface of the film is significantly smoother than the substrate surface. Apparently the energetics of the 2212 growth are such that it is energetically costly to disrupt the bounding BiO planes.

The healing of defects at the 2212/$SrTiO_3$ interface is in contrast to the propagation of roughness which is often observed in other epitaxial systems like Ge/Si[12] and GaAs/AlAs.[13] In some cases the distribution of defects on the surface of epitaxial films will be a replica of defects at the film-substrate interface. The shape of substrate-surface defects can even be propagated through the entirety of thick multilayer films.[13] Propagative roughness is minimized in multilayers meant for x-ray mirror applications by using an amorphous material as one of the constituents. For example, in Nb/Si and Mo/Si multilayers, TEM studies have shown that the crystalline transition metal layers have rough surfaces, but that the surfaces of the amorphous Si layer above them are considerably flatter.[14] Presumably healing occurs in the amorphous layer because the energetic cost of distorting local bonding to accomodate interface roughness is less than in the crystalline layers. The surprising aspect of the 2212 overgrowth on $SrTiO_3$ is that the roughness of the substrate is healed within a crystalline layer rather than an amorphous one. The image suggests that there is less of an energetic penalty associated with disrupting the stacking of the BiO and CuO layers than with bending them. This assertion is consistent with the ability to grow BSSCO-family materials with a varying number of CuO and Ca layers.

The strong tendency in the BiSrCaCuO materials to form continuous, straight BiO planes likely contributes to the success of the ALL-MBE technique with these materials. The naturally occurring layering in the BiSrCaCuO superconductors may be favorable for techniques which sequentially deposit the constituents, as ALL-MBE does. Efforts to grow the less anisotropic $YBa_2Cu_3O_7$ superconductors using a similar technique have been less successful.[15]

The non-conformal growth of the 2212 may mean that coverage of lithographically patterned steps in possible superconducting microcircuits may be a problem. On the other hand, the insensitivity of the 2212 growth to the quality of the substrate surface undoubtedly means that substrate preparation techniques need be less stringent in this materials system than in many others. For example, high-quality overgrowth of Fe on Ag substrates requires painstaking surface preparation because the vertical mismatch of the Fe and Ag lattice constants causes disruption of the first three to four Fe monolayers at atomic steps on the substrate.[16] This disturbance occurs despite the good in-plane lattice match of Fe and Ag. The short range of the disruption of 2212 growth at asperities on the $SrTiO_3$ surface is further evidence of the inherently anisotropic nature of the 2212 compound.

B. 2201/2212 Superlattices

The precise and rapid changes in stoichiometry that are possible with ALL-MBE allow growth of 2201/2212 superlattices with alternating molecular units of the two constituents. Each molecular unit is a half-unit-cell of the full crystal structure. A cross-sectional TEM image of a 2201/2212 superlattice grown on $SrTiO_3$ is shown in Figure 2. Superimposed on the micrograph are image simulations for 2201 and 2212 that were produced with the same focus and thickness parameters. Qualitative agreement between the calculated images and the micrograph is quite good. Image simulations with a variety of focus and thickness values convincingly demonstrate that the bright lines bounded with dark regions are the BiO double layers of 2212.

The high crystal quality of the 2201/2212 superlattice is not surprising given the good lattice match between the two phases. What is striking in Figure 2 is the layering of the 2201 and 2212, as is evident from the alternation of their respective 12.3Å and 15.4 Å molecular layer thicknesses. X-ray diffraction studies have previously given evidence for highly ordered growth of 2201/2223 multilayers with alternating half unit cells of the two constituents.[8] The low frequency of incomplete layers or pinhole-type defects supports the previously published interpretation of transport data on 2201/2212 superlattices, which showed that the superconducting transition temperature T_c was not strongly dependent on 2201 layer thickness.[6] The long lateral continuity of the single molecular layers in this image confirms the assertion that the 2212 layers in the superlattices are well isolated from one another by the intervening layers of 2201. The weak dependence of the 2201/2212 multilayer T_c on the thickness of the lower-T_c 2201 phase is therefore strong evidence of the two-dimensional nature of superconductivity in 2212.[6] The two-dimensional character of the superconductivity mirrors the anisotropic nature of the crystal structure.

C. 2212/2278 Heterostructures

A major advantage of the ALL-MBE method of film deposition is that its precise control of layering makes possible the growth of BiSrCaCuO phases which are not bulk equilibrium phases. For example, ALL-MBE has previously been used to grow films of the 2234 and 2245 compounds.[8] The non-equilibrium BiSrCaCuO phases have the bounding double BiO and single SrO layers that 2212 has, but the number of CaCuO2 units internal to the unit cell may be varied in a large range as long as the unstable layer is epitaxially stabilized by growth on 2212.[17] Figure 3 shows the proposed crystal structure of the 2278 phase and the well-known structure of 2212 for comparison. The c-axis lattice constant of 2278 is calculated to be 71.2 Å by assuming that all interplanar distances are the same as in 2212. This assumption is probably not exact due to the different charge-balance in 2278. In addition to growing non-equilibrium $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ phases, layers with only one bounding BiO layer have also been deposited which have the stoichiometry $Bi1Sr_2Ca_{n-1}Cu_nO_{2n+3}$.[17] Thus a Bi-1278 layer can be grown in a similar fashion to Bi-2278.

X-ray diffraction has been used to provide evidence for the successful growth of several of these higher-n phases.[8] Figure 4 shows a layer of the 2278 (n=7) material sandwiched between two thick films of 2212. While examination of TEM images is an inexact method of lattice constant determination, the figure shows that the layer spacing of the 2212 layers (15.4 Å) is slightly less than half the thickness of the nominal 2278 layer, which is calculated to be 35.6 Å thick. The 2278 phase is of considerable interest because when doped with Dy it is useful as a tunnel barrier in Josephson junctions.[4] 2278 and 1278 are also superconducting in their own right.[17,18]

TEM cross-sectional images (not shown) have also been taken of nominal 1278 tunnel barriers. The nominal layer thickness of 1278 (which should be a simple tetragonal rather than a body-centered tetragonal structure) is calculated to be 32.5 Å. It was not possible from TEM to distinguish them from the 2278 barriers and to determine whether a single BiO layer structure has actually been achieved. A microscopy technique which provides elemental contrast[19] may be necessary to get at this information or to determine the rare-earth-atom spatial distribution in the Dy-doped barrier layers. At this stage it is possible to report only that the transport properties of tunnel junctions with 2278 and 1278 barriers are quite different.[17]

D. Defects in 2212-based Heterostructures

The crystal quality of 2201 and 2212 films grown on a $SrTiO_3$ substrate by ALL-MBE is very high, as described above. The only defects which are commonly observed in these films are twin boundaries, one of which is shown in Figure 5. Part of the image has the 2212 a-axis oriented normal to the plane of the paper; this portion appears to have long, unbroken BiO planes. The other part of the image has the 2212 b-axis oriented normal. The b-axis-oriented portion of the image displays the incommensurate modulation which has previously been observed in 2212 films.[20] It has been shown that the growth of untwinned films via ALL-MBE is possible by using specially miscut substrates.[21] However, the special precautions necessary to prevent twinning are not deemed to be worthwhile for routine growths since the presence of twins is not believed to affect the performance of Josephson junctions.

Occasionally more troublesome defects may occur. These defects include stacking faults and antiphase boundaries, as Figure 6 illustrates. The stacking fault defects are most easily visualized by observing the presence of the wrong number of BiO planes, although presumably the SrO planes and $CaCuO_2$ planes may also be affected. There are several places in the image of Figure 6 where apparently more than two BiO planes occur together. Nearby in the image, an arrow points to the spot where layer spacings indicate that two phases of different stoichiometry have grown together. Estimates of the layer thicknesses for these phases indicate that they may correspond to 2223, which has an extra $CaCuO_2$ slab, and 3312, which has an extra BiO-SrO unit.[7] Exactly why these off-stoichiometric phases and stacking fault defects occur has not yet been determined. For reasons which are not well-understood, the frequency of occurrence of these defects is greater above a 2278 or 1278 barrier than in a 2212 film grown on a 2201 buffer layer. It may be hypothesized that the unfavorable charge balance in the unstable barrrier layer[17] may cause havoc in subsequent overgrowths.

RBS, EDAX and SIMS measurements indicate that the overall composition of the films is within a few percent of the nominal stoichiometry. However, defects which are visible on the surface of the superconducting films with optical microscopy are found by RBS, SIMS and EDAX to have a substantially different stoichiometry.[7] These surface defects typically occur in the corners of the films, where the deviation from the nominal stoichiometry would be expected to be greatest because the thermal effusion sources are not exactly on-axis. A correlation between the occurrence of these defects and poor Josephson junction performance has been observed.[7] Whether any of the defects which are visible in plan view with optical microscopy are identifiable with the defects seen in TEM cross-sections is not yet clear. The length scale of the the stacking faults and antiphase boundaries which are observed in cross-section is angstroms, while the size of optically observable surface defects is microns. Nonetheless, it may be that the nanoscale imperfections in film structure serve as nucleation points for the larger defects which are observed in plan view.

Despite the presence of planar defects and twins in the BiSrCaCuO films, the overall impression that TEM observations leave is one of a high degree of ordering. The low-magnification TEM image shown in Figure 7 illustrates this point. The bright layers in the image are three barrier layers, each designed to consist of a single molecular layer of 2278. Clearly these barriers are continuous over very large in-plane lengths, perhaps 1000 Å. The in-plane continuity of the barriers is clearly larger than that out-of-plane, once again illustrating the inherent anisotropy of BiSrCaCuO growth. An estimate of the average film non-stoichiometry can be made from an enlarged version of the image in Figure 7 by comparing the observed total thickness of the film to the thickness of a perfect film with the same layering sequence. The comparison shows that the Bi:Cu ratio of the film deviates from the target composition by only about 1%. The thickness is determined by the Bi:Cu ratio since it is this ratio that determines which of the BiSrCaCuO compounds is formed.

IV. CONCLUSIONS

Transmission electron microscopy is uniquely powerful when it comes to imaging point or line defects in a solid, or when one wants to image the structure of a single molecular layer in a film. Thus, TEM provides information about buried, localized features of thin films which is difficult to obtain in any other fashion.

The TEM images taken as part of this study have strikingly confirmed previous hypotheses about the structure of heterostructures and multilayers grown with the ALL-MBE technique. In particular, the TEM images demonstrate that single layers of 2212 and 2201 can be grown as part of a multilayer. Furthermore, single layers of metastable or unstable phases such as 2278 and 1278 can also be grown. These TEM micrographs provide the first direct evidence for the existence of these phases. While growth flaws like twins, stacking faults and antiphase boundaries do occur, especially in overgrowths on metastable barrier layers, the images are most notable for the long, unbroken continuity of most 2212 planes. Up to this point, ALL-MBE growth of BiSrCaCuO superconductors have not reached the perfection that is observed in MBE growth of GaAs, AlAs and related compounds. However, planned improvements in the ALL-MBE process such as rotation of the substrate during growth may make comparably low defect densities possible.

The TEM images presented here support previous ideas about the two-dimensional nature of superconductivity in the 2212 compound.[6] In addition, they provide new information about the ways in which growth of inherently highly anisotropic phases may differ from growth of cubic materials. Studies of the growth of high-temperature superconductors may in the end have as much to teach us about anisotropic solids as about the fundamental nature of superconductivity.

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FIGURES

FIG. 1. A high-resolution cross-sectional TEM image showing overgrowth of a 2212 superconductor film on a $SrTiO_3$ substrate (001) surface. The view is along the (100) axis of the $SrTiO_3$ substrate. Registry between planes in the substrate and overlayer is nearly perfect, resulting in a coherent interface. The BiO planes are continuous throughout the image, even directly above rough areas on the $SrTiO_3$ surface.

FIG. 2. A high-resolution cross-sectional TEM image of a 2201/2212 superlattice. The view is along the (001) axis of the $SrTiO_3$ substrate. The alternation of the 15.4 Å period of 2212 and the 12.3 Å period of 2201 is readily identifiable. Also shown are image simulations of 2212 and 2201 which were calculated using the known lattice constants of the materials. Parameters for the simulations are focus = -450, thickness = 200Å.

FIG. 3. Hypothetical crystal structure of the Bi-2278. The c-axis lattice constant is 71.2 Å, so the thickness of a single layer should be 35.6 Å. The in-plane lattice constants are assumed to be the same as in 2212. The view is along the (001) axis. Shown for comparison is the well-known crystal structure of the 2212 phase.

FIG. 4. High-resolution cross-sectional image of a 2278 barrier layer sandwiched between two thick films of 2212. The view is along the (001) axis of the $SrTiO_3$ substrate.

FIG. 5. High-resolution cross-sectional image of a twinned section of a 2212 film. The layers on the right-hand side of the image have the b-axis normal to the plane of the figure and show incommensurate modulation. Layers on the left-hand side have the a-axis normal to the plane of the figure.

FIG. 6. Stacking defects in a 2212 film grown on $SrTiO_3$ substrate. View is along the (001) axis of the $SrTiO_3$ substrate. The antiphase boundary is indicated by a black arrow.

FIG. 7. Low-resolution micrograph of a BiSrCaCuO film with three barriers each consisting of a single molecular layer of 2278, separated by thicker layers of 2212. This image demonstrates the long lateral coherence length which is typically observed in BiSrCaCuO-based heterostructures grown by ALL-MBE.