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NON-STOICHIOMETRIC DEFECTS IN YBaCuO THIN FILMS

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Because the growth of YBaCuO thin films is often carried out under non-equilibrium conditions, most films are highly defected. This has important practical implications for superconducting transport properties. For example, a dramatic increase in intragrain critical current density has recently been reported for YBa₂Cu₃O₇ containing a fine dispersion of double CuO layer structures. These and other crystallographic defects can be introduced during the YBa₂Cu₄O₈ to YBa₂Cu₃O₇ phase transformation, when local deviation from ideal, single-phase stoichiometry occurs. Therefore, a thorough understanding of the mechanism of formation and growth of a new phase within an existing one in the YBaCuO system is required.

The strain associated with the transformations between related phases in the YBaCuO system can be effectively accommodated at free surfaces and grain boundaries. Thus it is expected that these planar defects will readily act as heterogeneous nucleation sites. In the present study, high resolution transmission electron microscopy (TEM) images are obtained from cross sections of thin films nominally deposited as c-oriented YBa₂Cu₃O₇ on magnesium oxide and lanthanum titanate (LaTiO₃) substrates. These images show that at many locations in such specimens, the double CuO layer (YBa₂Cu₄O₈) structure indeed appears to originate at external surfaces, typically propagating a short distance (~100Å) into a film where the interior is found to have the single CuO layer (YBa₂Cu₃O₇) structure

Relating deposition conditions to the extent of double CuO layer formation helps to establish the mechanism by which CuO planes move into and out of the crystal structure during phase transformations in YBaCuO, and in particular to gain insight into the details of the diffusion involved. Computer simulations which model transformations in YBaCuO using a copper-oxygen intercalation scheme have been performed to elucidate these mechanisms.

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Defects in superconducting YBaCuO thin films deposited by laser ablation are investigated by high resolution transmission electron microscopy. Micrographs reveal numerous defects in the YBaCuO film, falling into four basic classes. One of these is an interesting, non-stoichiometric helical defect structure which possibly corresponds to a growth-related screw dislocation. In general, defects in the YBaCuO film are associated both with growth geometry and with local deviations in stoichiometry. Substrate surface geometry is seen to have a profound effect on the number and type of defects produced. Simulation of annealing transformations using a static lattice, three dimensional, Monte Carlo technique is carried out to gain further insight into specific defect formation mechanisms. The results of these studies suggest preparation conditions that are expected to lead to films with improved critical current densities.

1. INTRODUCTION

Because the growth of YBaCuO thin films is typically carried out under non-equilibrium conditions, most films are highly defected. However, YBaCuO films generally show transport properties superior to more perfectly crystalline bulk material.¹ Understanding the relation between crystallographic defects and electrical properties in superconducting YBaCuO therefore has important practical implications, as low critical current density values presently stand as one of the important obstacles in the way of more widespread application of high- T_c oxide superconductors.

In addition, detailed characterization of defects may lead to insights on film growth processes. For example, it has been found that extrinsic stacking faults in the CuO layers of the YBaCuO structure can be introduced during the YBa₂Cu₄O₈ to YBa₂Cu₃O₇ phase transformation, when local deviation from ideal, single-phase stoichiometry occurs.² A dramatic increase in intragrain critical current density has recently been reported for YBa₂Cu₃O₇ containing a fine dispersion of these double CuO layer structures.³ Therefore, control of this type of defect (either producing or preventing it) requires a thorough understanding of the kinetics of phase transformations in the YBaCuO system. Many other defects also form in such a way as to accommodate local deviations in stoichiometry, and attention is focused on these in the present study, since film composition during deposition is an area where improvements in process control can be made.

2. EXPERIMENTAL PROCEDURE

In the present study, high resolution transmission electron microscopy (TEM) images are used to study thin films of superconducting YBaCuO. The films were nominally deposited as c-oriented YBa₂Cu₃O₇ on

(100)-oriented magnesium oxide (MgO) and (1 $\bar{1}$ 02)-oriented alumina (Al₂O₃) substrates. Deposition was carried out using laser ablation at 200mTorr oxygen pressure and a substrate temperature of 750°C. A buffer layer of approximately 100Å CaTiO₃ was deposited on the alumina substrates before growth of the YBaCuO film was initiated. The YBaCuO layers were typically 300nm thick and had critical current densities on the order of 1 to 2x10⁶ A/cm² at 74 K (as measured by the ac mutual inductance response of the films).⁴

Cross-sectional specimens for TEM were prepared by non-reactive ion milling at 5.0 to 5.5 kV, followed by a low-angle final thinning at approximately 4 kV. Subsequent TEM imaging was carried out using a JEOL JEM200CX operating at 200kV and the Berkeley Atomic Resolution Microscope operating at 800kV. The NCEMSS software package⁵ developed at the National Center for Electron Microscopy was used for simulation of high-resolution TEM images.

3. EXPERIMENTAL RESULTS

Computer simulation of high-resolution TEM images shows that, at optimum defocus and proper crystal orientation, the CuO planes in the YBa₂Cu₃O₇ structure produce bright white contrast and the heavy cations (Y and BaO layers) appear as prominent black dots, while the CuO₂ planes show almost no contrast. The actual TEM images show a proliferation of defects of many types throughout the films examined. The films deposited on Al₂O₃ with CaTiO₃ buffer layer are notably poorer in quality than those deposited on MgO substrates, exhibiting extremely high defect densities, including pockets of amorphous material in the film. This can be attributed in part to the nature of the buffer layer, which is polycrystalline with some surface irregularity.

At many locations in the specimens, double CuO layers (YBa₂Cu₄O₈ structure) appear as isolated stacking defects (with displacement $R=1/6[031]$ ⁶), typically extending a short distance (50–100 Å) within a matrix of material that is predominantly found to have the single CuO layer (YBa₂Cu₃O₇) structure. An example of this is shown in Figure 1, where no less than six CuO-related stacking faults can be seen. An unusual occurrence also appears in this figure, where a step in the interface is just the correct height to accommodate one additional YBaCuO unit cell. As a result, registry of all lattice planes is maintained in the film below this point; no defects are introduced in the YBaCuO, although a roughly semicircular strain field is visible as a dark band of contrast. An additional example of the presence of double CuO layers is shown in Figure 2. Here the copper and oxygen content are locally higher than was the case in Figure 1, and the average stoichiometry approaches YBa₂Cu_{3.5}O_{7.5} (or Y₂Ba₄Cu₇O₁₅, the "2-4-7" phase⁷⁻⁹) in the region near the edge of the specimen.

Another stacking defect observed in one instance involves the heavy cations rather than the CuO planes. Since the stacking of heavy cations in YBa₂Cu₃O₇ follows the sequence Ba-Y-Ba, a high-resolution image will show three black dots in each unit cell of the 1-2-3 structure. However, in Figure 3, there is a region where a YBaCuO unit cell can be seen which is wider than those of the YBa₂Cu₃O₇ material surrounding it and contains four rows of heavy cations, indicating the presence of an extra Y or BaO layer.

In general, irregularities in the substrate surface were found to generate a series of defects in the YBaCuO films, appearing as a type of antiphase boundary between two mis-matched regions of the crystal. As shown in Figure 4, there are many instances where lattice planes bifurcate at such boundaries, and thus these defects become sites for the accommodation of non-stoichiometry in the film. Crystallographic defects, especially dislocations, in the substrate material have been observed to result in this same type of boundary in the YBaCuO film.¹⁰

A very interesting defect structure of a different type can be seen in Figure 5. One possible interpretation of this image is that a type of screw dislocation, helical in shape, intersects the surface of the specimen at the point where the defect is visible. It can be seen that over part of its extent, the defect has produced a displacement whose component in the plane of the figure is $1/3[001]$. In addition, the pitch of the dislocation "helix" is not constant, indicating that the defect is a non-conservative one (i.e., that it incorporates changes in stoichiometry).

4. COMPUTER MODELING

Of the many non-stoichiometric defects that arise in the YBaCuO system, one of the most significant with

respect to the superconducting properties is the CuO stacking faults which occur as a result of deviations in the amount of CuO near the basal plane. Therefore, in order to better understand how to control the number, density, and distribution of such defects as a function of deposition parameters and post-deposition annealing, phase transformations leading to their formation are studied by developing a static lattice, three dimensional Monte Carlo simulation. The simulation is based on an intercalation scheme, and the details of this are reported elsewhere.^{11,12}

Changes in CuO content in the YBaCuO system generate a series of layered structures, $\text{Y}_2\text{Ba}_4\text{Cu}_6+\text{xO}_{14+\text{x}}$, where $\text{x}=0$ corresponds to the well known $\text{YBa}_2\text{Cu}_3\text{O}_7$ (1-2-3) phase. An examination of the evolution of microstructures during the transformation that occurs when x is varied from 0 to 1 by increasing the partial pressure of oxygen in a material with excess copper present indicates that the transformation is heterogeneously nucleated at existing grain boundaries and surfaces within the material as can be seen in the simulation snapshot shown in Figure 6. Due to the elastic compensation available at surfaces and grain boundaries, the resulting extra-layer defects are effectively pinned and hence are not observed to move far into the grain interior. This results in an inhomogeneous distribution of these beneficial stacking faults. When a transformation is induced by increasing x , an additional factor limiting the extent of double CuO layer formation is the ability of the system to deliver copper to grain boundaries and free surfaces.

A better distribution of defects is produced in the simulation by inducing the 1-2-4 to 1-2-3 and 2-4-7 to 1-2-3 transformations, where x is decreasing rather increasing. A study of the kinetic evolution of microstructures during these transformations reveals that CuO diffuses outward to grain boundaries and surfaces. However, due to microstructural and elastic inhomogeneities present in the film and induced by the motion of CuO planes out of the grain interior, many remnant double CuO layers are retained producing a much more homogeneous distribution of defects throughout the film than was created by the reverse transformation. Thus it is expected that films prepared with a nominal cation stoichiometry equal to 2-4-7 and then ex-situ annealed under conditions where the 1-2-3 phase is stable should produce films with superior critical current densities. In addition, films with a moderate distribution of grain boundaries and planar defects are expected to produce a more homogeneous distribution of the CuO layer defects than single crystal films as boundaries and surfaces are required throughout the film for outward diffusion of copper and oxygen.

5. DISCUSSION

The heavy-cation stacking fault seen in Figure 2 consists of either an extra Y plane or an extra BaO plane in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure. The presence in YBaCuO films of a structure corresponding to the addition of an yttrium plane has in fact been reported by Ramesh *et al.*¹³ This group used detailed simulation of high-resolution TEM images to distinguish the addition of a Y plane from that of a BaO plane, and concludes that the defect stoichiometry is $\text{Y}_2\text{Ba}_2\text{Cu}_4\text{O}_9$ (a "2-2-4" structure). Therefore, it is likely that the defect observed in the present study also corresponds to $\text{Y}_2\text{Ba}_2\text{Cu}_4\text{O}_9$. It should be noted, however, that the work by Ramesh *et al.* also suggests that the addition of a BaO plane to the $\text{YBa}_2\text{Cu}_3\text{O}_7$ structure also occurs, though less frequently than the 2-2-4 defect. The presence of CuO stacking faults is thought to enhance critical current density in YBaCuO, and this idea is further supported by the close match between the typical fault size and the superconducting coherence lengths in the 1-2-3 phase of YBaCuO (both within the a-b plane and perpendicular to it)¹⁴, indicating that the faults should act as effective flux pinning sites.^{14,15} Because of its geometrical similarity, the heavy cation stacking defect observed here may be another type of potential flux pinning site (though the electrical properties of the 2-2-4 material are unknown at present).

A recently published study¹⁶ using scanning tunneling microscopy (STM) shows that YBaCuO films can grow by means of an island mechanism, with each island consisting of a series of expanding spiral ledges surrounding a screw dislocation core. In light of this classic growth mechanism, first proposed by Frank¹⁷, the interpretation of the image in Figure 5 as a type of screw dislocation is particularly attractive. The dimensions of the dislocation core are comparable to the YBaCuO coherence length in the a-b plane, and thus these defects are also expected to contribute to flux pinning (especially since the dislocations extend through the entire thickness of the film). It should be noted that, based on a single image, it is impossible to conclusively determine the nature of a defect as complex as that shown. Nevertheless, the appearance of this image allows us to form a hypothesis which suggests a direction for future study investigating the actual structure of this helical defect and its possible role in the film growth mechanism.

It is of course expected that the geometry of the surface will influence the growth of a film, and from the high resolution TEM images, it is clear that this is indeed the case. What is interesting to note in the present

context, however, is that the defects generated by irregularities in the interface surface are not always only structural in nature. As seen in this study, there are many defects present which also serve to incorporate deviations in the stoichiometry of a YBaCuO film. The substrate surface is also important in determining how a film grows, since surface steps and other features are preferred nucleation sites for film formation and may in fact serve as the source of screw dislocations produced during growth

6. SUMMARY AND CONCLUSIONS

The non-stoichiometric defects observed in YBaCuO films can be classified into four types: CuO stacking faults, Y (or BaO) stacking faults, complex, helical defects, and non-stoichiometric "mismatch" boundaries. Of these, the first three types apparently have the potential to act as flux pinning sites in YBaCuO while mismatch boundaries, grain boundaries and other types of defects are detrimental to superconductivity. Thus, control of defect type and density in a film is essential for desired electrical properties. Achieving this control depends critically on both maintaining stoichiometry during deposition and on preparation of the substrate surface.

The combination of high resolution TEM imaging and computer simulations leads to an interplay of results which has proved extremely useful for the study of defects in YBaCuO thin films. TEM provides an experimental basis for the development of microscopic models of growth kinetics. Computer simulation of these models then provides the time resolution and control over "fabrication" conditions necessary to investigate the effects of transformation kinetics on defect formation. Simulations of transformations leading to the development of flux pinning CuO extrinsic stacking faults suggest specific ex-situ annealing conditions for producing films with improved superconducting properties. More detailed characterization of the possible screw dislocation observed here is needed in order to gain more information on growth mechanisms of YBaCuO films.

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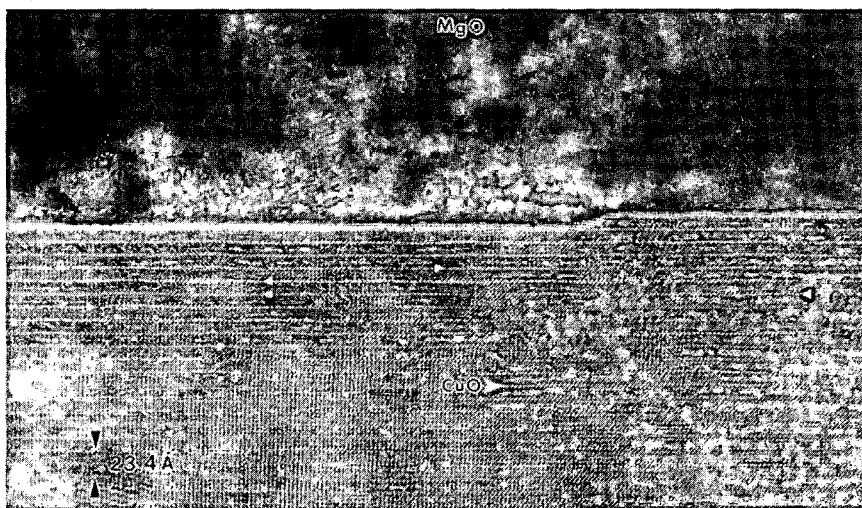


Figure 1: High resolution TEM image of YBaCuO on MgO, showing CuO stacking faults (small arrowheads) and an interface step which accommodates exactly one additional YBaCuO unit cell.

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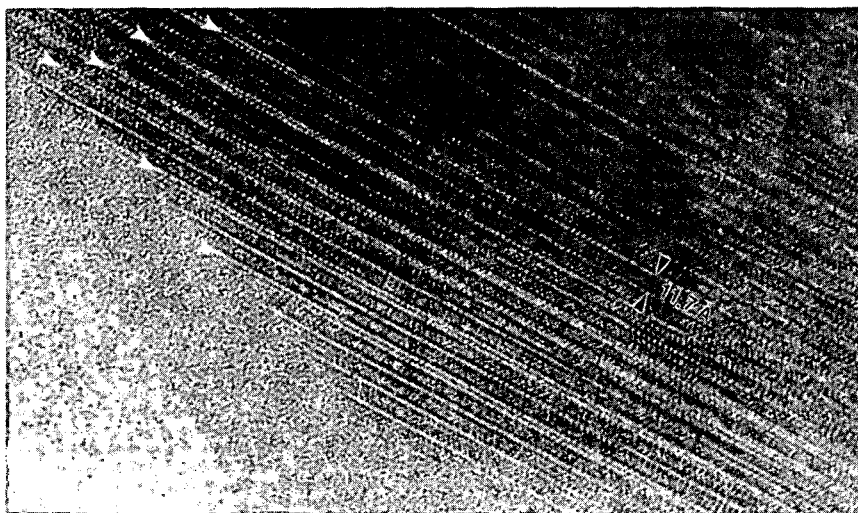


Figure 2: Additional CuO double layers (white arrows), more extended than those in Figure 1. The overall stoichiometry deviates appreciably from $\text{YBa}_2\text{Cu}_3\text{O}_7$ in this region.

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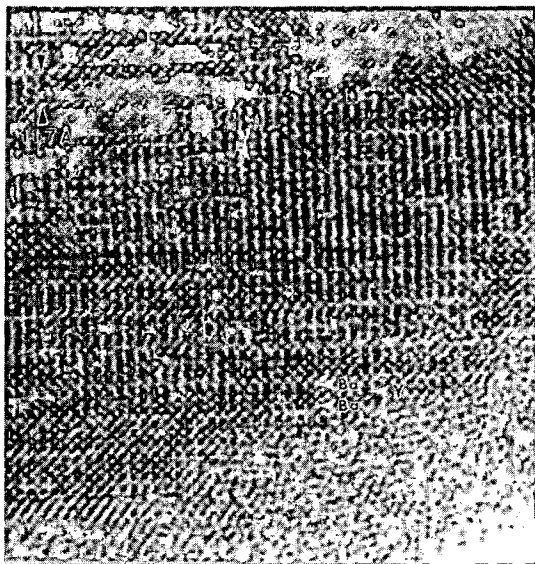


Figure 3: Y or BaO stacking fault (indicated by arrow). This defect most likely corresponds to the $Y_2Ba_2Cu_4O_9$ structure of YBaCuO.

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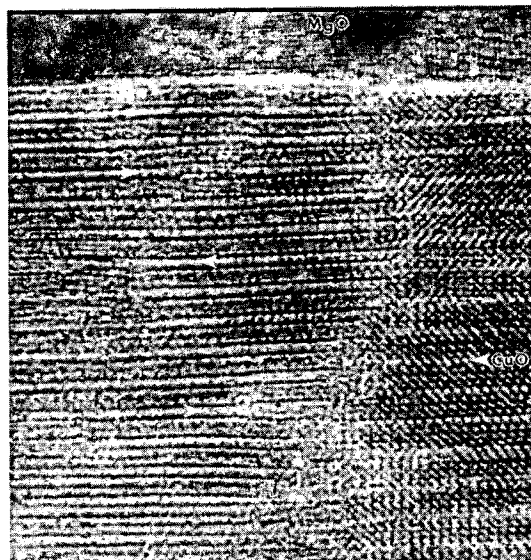


Figure 4: "Mismatch" boundary in YBaCuO film, generated by small step in the interface surface. Non-stoichiometry can be seen where atomic planes begin to split or bifurcate (arrows).

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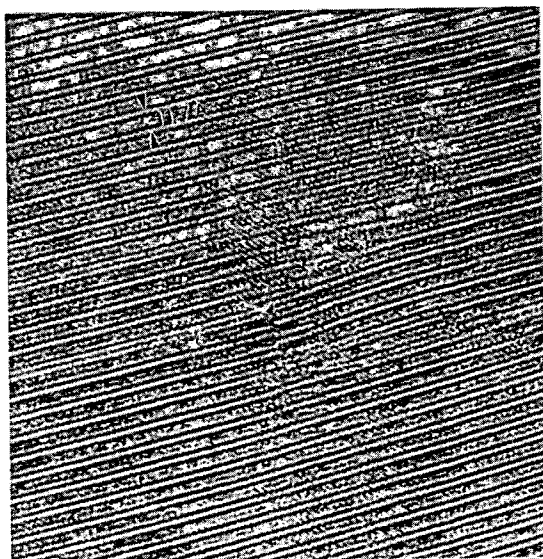


Figure 5: Complex, helical defect in YBaCuO film, possibly interpreted as a non-conservative screw dislocation produced as a result of a spiral growth mechanism. The presence of some double CuO layers can also be seen in this region.

XBL 916-1133

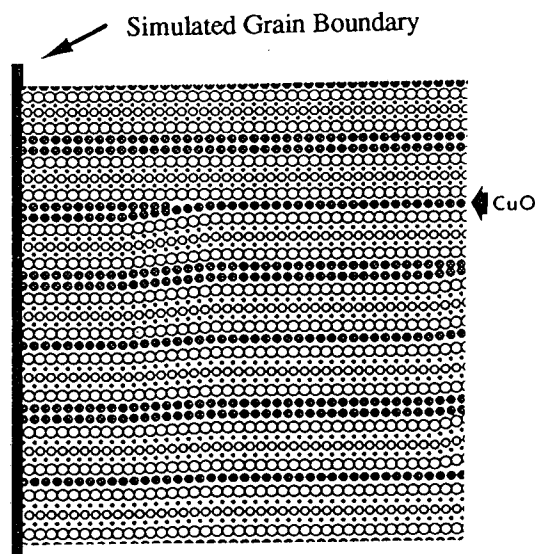


Figure 6: Kinetic "snapshot" obtained by Monte Carlo simulation of CuO (black circles) intercalation from simulated grain boundaries. Here the overall composition is close to $Y_2Ba_4Cu_7O_{15}$ and planar defects similar to those in Figures 1 and 2 can be seen.

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