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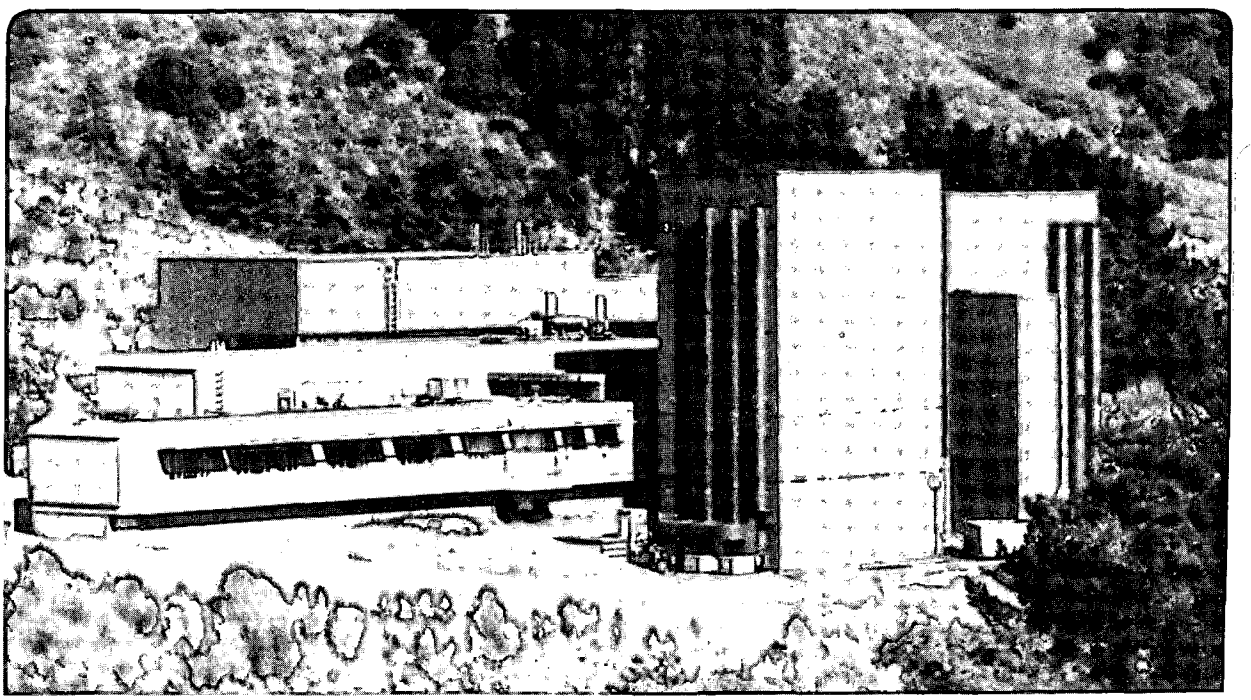

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C. Burmester, L. Wille*, and R. Gronsky

Materials Science Division
National Center for Electron Microscopy
Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

*Florida Atlantic University
Dept. of Physics
Boca Raton, FL 323431

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Computer Modeling of Y-Ba-Cu-O Thin Film Deposition and Growth

C.P. Burmester[1,2], L.T. Wille[3], and R. Gronsky[2,4]

[1]Materials Science Division, Lawrence Berkeley Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA.
[2]Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720, USA.
[3]Department of Physics, Florida Atlantic University, Boca Raton, FL 33431, USA.
[4]National Center for Electron Microscopy, Lawrence Berkeley Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA.

The deposition and growth of epitaxial thin films of $YBa_2Cu_3O_7$ are modeled by means of Monte Carlo simulations of the deposition and diffusion of Y, Ba, and Cu oxide particles. This complements existing experimental characterization techniques to allow the study of kinetic phenomena expected to play a dominant role in the inherently non-equilibrium thin film deposition process. Surface morphologies and defect structures obtained in the simulated films are found to closely resemble those observed experimentally. A systematic study of the effects of deposition rate and substrate temperature during in-situ film fabrication reveals that the kinetics of film growth can readily dominate the structural formation of the thin film.

INTRODUCTION

Bulk studies of the $YBa_2Cu_3O_z$ high T_c oxide superconductor have made significant progress in the last few years in improving engineering properties. However, bulk polycrystalline materials still have less than adequate properties to motivate commercial application, in part due to weak superconducting links between grains.[1] In contrast, thin films of this material allow the production of highly oriented and textured material as well as providing a greater degree of control over the interior microstructure. Thus, the first viable applications promise to be in the area of microelectronic devices utilizing thin films of the YBaCuO superconductor.[2] Thin film deposition, however, is an inherently non-equilibrium process and thus a true understanding and, more importantly, control of the structural characteristics and properties of YBaCuO thin film will be best pursued through an understanding of the kinetic processes dominant during deposition. The evolution of non-equilibrium systems is expected to be strongly influenced by impurities and by surface inhomogeneities.[3] As a result, it is difficult to interpret experimental kinetic data as attributable to a specific macroscopic parameter as microscopic effects can easily dominate. In addition, most characterization techniques lack either sufficient time or spatial resolution necessary to allow study of the kinetic evolution of thin film structures. In many other systems, the problem of characterizing non-equilibrium evolution has been addressed by "enhancing" the resolution of experimental techniques with the effectively "infinite" time and spatial resolution of atomistic computer simulation. Computer simulation allows both the development and evaluation of microscopic theories of kinetic evolution and a degree of control over the "experimental" conditions inaccessible by experimental methods. Thus a technique for the computer modeling of thin film deposition and growth is introduced and its theoretical and experimental basis briefly described. The ability of this technique to model established trends is examined and results of the effects of deposition techniques on film characteristics are reported.

THEORETICAL BASIS

The simulation must be based on the predominant microscopic mechanisms operating during thin film deposition in order to mirror the rich range of fabrication conditions afforded

by deposition techniques. It is based on an extension of the Monte Carlo technique to model deposition, surface redistribution, and bulk realignment of deposited species. As the YBaCuO system can be described by a ternary phase diagram of yttrium, barium, and copper oxides,[4] the simulation "deposits" variable ratios of these oxides particles. Within a unit cell of a YBaCuO phase, each atom can be assigned a type and an orientation with respect to the substrate which reflects the crystallographic orientation of the domain it participates in within the thin film. In addition to the three oxide types, two additional particle types are used to represent the substrate and "unoccupied" sites. These unoccupied sites correspond to voids within the film and unoccupied sites above the current surface of the film. Amongst the yttrium, barium, and copper oxide particles, the pair interactions are taken over the six nearest neighbor sites in the lattice: four "in-plane" (001) sites and two "out-of-plane" [001] sites. These interactions are dependent on both type and direction and their magnitudes are chosen to reflect the in-plane clustering and out-of-plane layer ordering experimentally established for the layered YBaCuO superconductors. Oxide-substrate interactions vary in the same manner allowing the modeling of different substrate types and orientations. Thus the Hamiltonian describing the configurational energy of microstates arising under the simulated deposition process is composed of a generalized Ising model reflecting surface, vacancy/surface, and oxide interactions, coupled with a Heisenberg spin interaction reflecting the variation of interactions with particle misorientation. This Hamiltonian can be written in the compact form:

$$H = -\sum_{<i,j>} V_n(n_i)n_i n_j - \mu_i \sum_{<i>} n_i - \sum_{<i,j>} V_s(\theta_{ij})(s_i \cdot s_j)$$

where $n_i = 1,2,..,5$ denotes the type at site i, and $|s_i| = 1$. The chemical potential terms, μ, in the Ising model component of the Hamiltonian, while taken to be zero in this study, can be used to describe different deposition atmospheres above the film with respect to the different metallic species in the film. This is particularly useful in modeling the transformations that occur in the pseudo-binary subcomponent of the overall ternary system described by $Y_2Ba_4Cu_{6+x}O_{14+x}$.[5-8] In the current study, particles interact via symmetrical pair interactions $V_n V_s$ only. Thus a logical enhancement of this model might include multi-spin interactions.

The simulation employs three excitation mechanisms which model deposition, surface redistribution, and bulk realignment of oxide particles. The deposition step, an inherently open process, is carried out in the grand canonical scheme with Kawasaki dynamics.[3] The surface redistribution step, involving the exchange of nearest neighbor surface particles and vacancies, conserves the total number of particles in the film and is thus carried out in the canonical ensemble with Glauber dynamics.[3] Finally, the bulk realignment step involves the attempted orientation change of an oxide particle within the film. As the "orientation" property is not conserved under this step, orientation changes are calculated in the grand canonical scheme with Kawasaki dynamics.

The deposition rate for the simulation is defined as the number of deposition steps attempted divided by the total number of simulation steps attempted (deposition, surface redistribution, and bulk realignment steps). Thus, a deposition rate equal to 1 corresponds to pure deposition and no "annealing." In this way, in-situ vs. ex-situ thin film deposition schemes are modeled. During in-situ deposition, deposition and "annealing" (surface redistribution and bulk realignment) are carried out simultaneously in a ratio corresponding to the deposition rate selected for the current simulation. By contrast, during ex-situ deposition, all the deposition steps are carried out first, often producing amorphous films, after which the annealing steps are performed.

In this study, the substrate is chosen to be atomically smooth, defect free, and its interaction with the deposited material constant, attractive, and independent of crystallographic orientation so as to effectively eliminate the influence of the substrate from the study of the effects of other parameters. Deposited material is also taken to be fully oxygenated. In addition, the orientation vector of the deposited particles is constrained to the <100> unit cell

directions. Studies are in progress which remove these constraints in the study of substrate variations and the development of the full range of grain boundary and surface orientations.

SIMULATION RESULTS

Many hundreds of simulated films were produced under various deposition conditions. All films studied examined near substrate growth with typical lattice sizes consisting of $5x10^5$ $YBa_2Cu_3O_7$ unit cells. For a simulation lattice with toroidal boundary conditions in the [100] and [010] directions created such that its lateral dimensions are an order of magnitude greater than its vertical extent, this produced films approximately 15 nm thick. All films reported here were deposited with a cation ratio of 1:2:3 (Y:Ba:Cu) with a slight shortage of barium in order to produce stoichiometric $YBa_2Cu_3O_7$ thin films.

As the orientations of particles is constrained to the cube directions, individual domains within the film are found to fall into two general classes: domains whose unit cell [001] 'c' axis was oriented perpendicular to the substrate, or 'c' type, and domains whose 'a' or 'b' axis was oriented perpendicular to the substrate, or 'a' type.

By varying the conditions under which the films were produced, a broad range of orientation types and surface morphologies were observed. Ex-situ films of the 'a' type show surface morphologies composed of a network of [100] and [010] oriented lenticular shaped interlocking "bars" of YBCO material. The surface of such a film is shown in Figure 1a. The size of such domains was seen to coarsen upon increasing annealing times. Overall, ex-situ 'a' type film surfaces were found to be very "rough" and characterized by rectangular shaped protrusions of 'a' type material in which the height of the film surface from the substrate varies markedly from point to point. Domains were found to be commonly subdivided by pronounced anti-phase boundaries. In contrast, ex-situ films of the 'c' type (see Figure 1b) displayed a much more consistent surface height. The overall shape of the 'c' type domains was more circular in nature than the interlocked 'a' type domains, producing a "pebbly" morphology. Domains of anti-phase relation were similarly separated by anti-phase boundaries in the film surface. Surfaces of in-situ grown films displayed a much less dramatic surface structure. Surfaces were generally atomically smooth but domain and anti-phase boundaries were decorated with surface defects and depressions. These decoration patterns were often sufficient to identify the surface type as the pattern inscribed would be orthogonal and rectangular in nature for 'a' type surfaces and more curvelinear in nature for 'c' type surfaces. Numerous thin film studies describe surfaces or include surface micrographs of ex-situ[9-12] or in-situ[13,14] deposited films which display completely analogous features as those produced by the simulation.

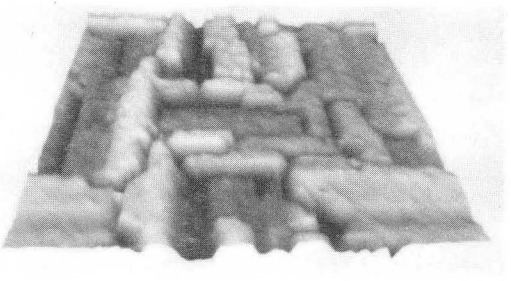

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Figure 1a: Surface structure of ex-situ grown thin film displaying 'a' type domains.

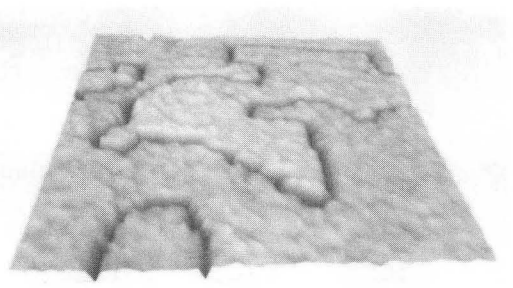

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Figure 1b: Surface structure of ex-situ grown thin film displaying 'c' type domains.

Under specific conditions, adjacent domains of 'c' type and 'a' type material can be observed to grow. The growth rate anisotropy between the 'a' and 'c' directions of the YBCO unit cell is apparent in the surface characteristics of such films. The greater growth rate of the 'a' type domains leads to regions of the film surface that are notably greater in vertical extent than adjacent 'c' type domains.

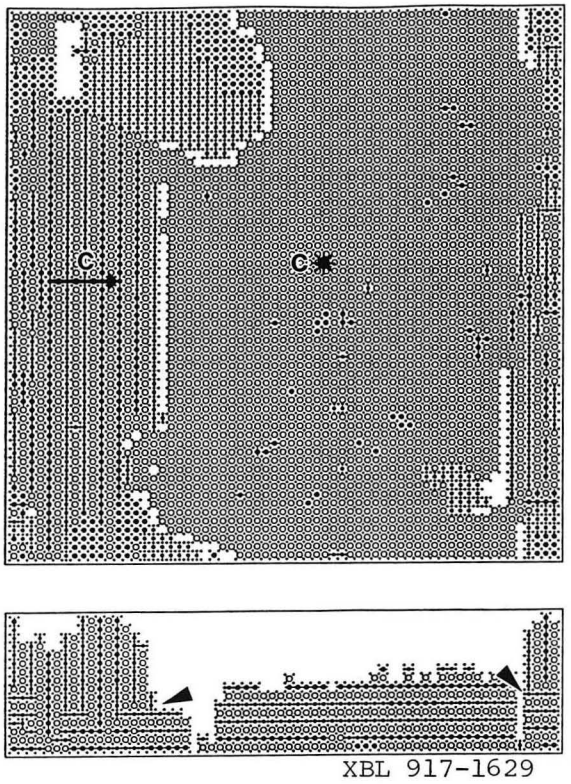

Figure 2: Plane (a) and cross-section (b) view of ex-situ grown film displaying both 'a' and 'c' type growth and an assortment of defects.

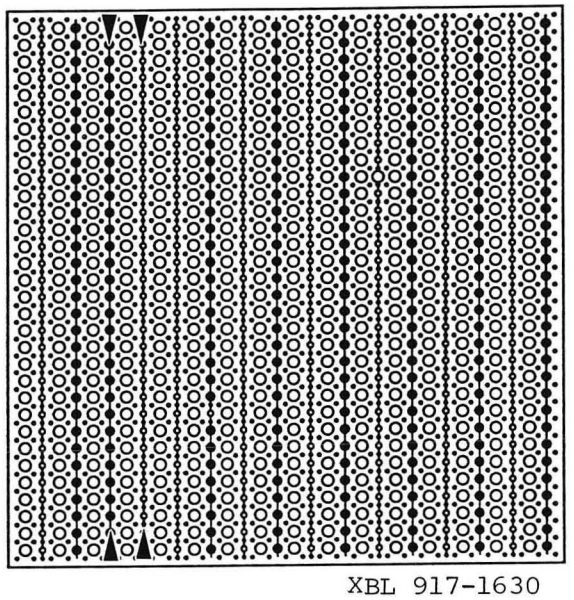

Figure 3: Plane section of an nearly perfect in-situ grown film illustrating a growth layer defect. Large filled circles represent barium, medium open circles yttrium, small open circles oxygen in the CuO basal plane, and small filled dots, copper. The lines included delineate the [100] or [010] directions.

Many different types of defects were found to occur in the simulated thin films as shown in the cross-sectional and planar slices of Figures 2 and 3. Growth defects include stacking faults in which two layers were observed to switch position in a unit cell, for example, the exchange of a CuO and Y layer, may be observed in the nearly perfect in-situ grown film depicted in Figure 3. Additional defects of this type are illustrated in both plane and cross-section in Figure 2. An anti-phase boundary delineates a small circular subdomain in the upper left hand portion of Figure 2a within the broad central 'c' type domain. Within the subdomain, a layer defect is visable where a Y layer changes to a CuO layer. The domain boundary between the 'c' and 'a' type regions of this film is sharply delineated by a surface groove when running along the <100> type directions, but inclined boundaries of the <110> type seem more easily accommodated and do not retain vacancies at the boundary. In general, growth layer defects, as opposed to anti-phase defects and orthogonal grain boundaries, were more easily accommodated by the film. Through the film thickness, domain boundaries between orthogonal domains are a common occurrence and are often found to retain deviations from stoichiometry, as observed in the cross-section of Figure 2b. The surface variation of the cross-section of Figure 2 is similar to those reported by cross-sectional TEM studies.[15] Point defect inclusions of oxide particles are typically observed on growth surfaces. In general, in-situ films grown with lower deposition rates and ex-situ films annealed for longer times

produced films of higher crystallographic homogeneity, as expected.

To investigate the effects of deposition rate and substrate temperature on the growth and orientation of in-situ grown films, a systematic study was performed under conditions where 'c' type growth is energetically preferred. In these studies, the effects of the substrate and the deposition atmosphere were held constant. In order to quantify the kinetic processes operating during deposition, the surface mobilities of particles on 'a' and 'c' type surfaces within the film were monitored. The results of these studies are depicted graphically in Figure 4. Figure 4a depicts the variation of the fraction of the film sites having a 'c' type orientation vs. deposition rate at constant simulation temperature of 0.8. At high deposition rates, the distribution of sites in 'c' and 'a' type orientations are nearly equal, reflecting the nearly amorphous nature of films produced under these conditions. As the deposition rate is decreased, the fraction of 'c' type growth gradually increases. In this range, the growth of films is nucleation limited and thus consist primarily of many small domains of 'c' type material. Note that the surface mobilities remain essentially equal throughout this region reflecting that a nucleation and not growth mechanism is predominant. However, as the deposition rate is decreased below 0.01, a sudden transformation to 'a' type growth occurs. This transformation to 'a' type growth occurs with a corresponding a drop in the surface mobility of 'a' type domains, and an increase in the mobilities of 'c' type domains. This bifurcation of the surface mobilities indicates a transition to growth limited kinetics and the lower 'a' surface mobilities reflect that more particles are adsorbing to 'a' type surfaces.

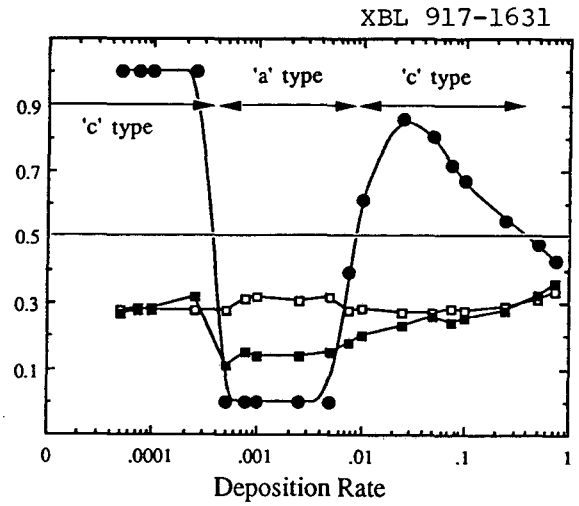

Figure 4a: A plot of film orientation and surface mobilities vs. deposition rate at constant temperature equal to 0.8. In both figures, filled circles represent fraction of 'c' type sites, filled squares 'a' surface mobilites, and open squares 'c' mobilities.

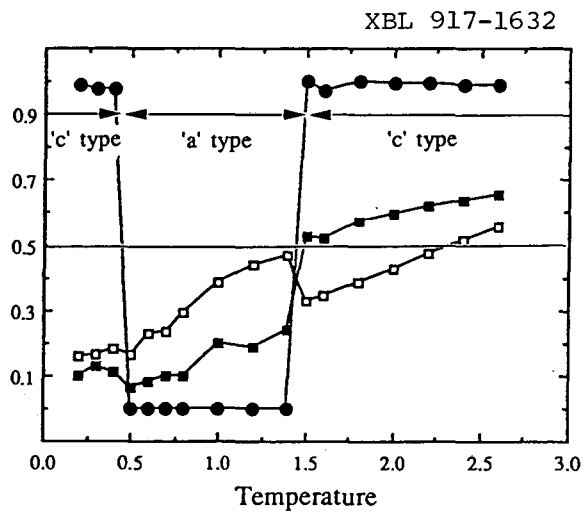

Figure 4b: A similar plot to 4a but varying temperature at constant deposition rate equal to 0.001.

While equilibrium considerations indicate that 'c' type growth should still prevail, the growth anisotropy between the 'a' and 'c' direction of the YBaCuO material allows provides 'a' type growth with a kinetically more favorable growth mechanism. It is felt that most thin film experiments are carried out in this regime. Substrate effects lead to the nucleation of 'c' type domains, but the growth limited kinetics quickly lead to the formation of 'a' type growth thus producing the type of 'c' to 'a' type transformation through thickness in thin films which is commonly reported[9,10,13-16] and also observed in Figure 2b. Under very low deposition rates, the trend is again seen to reverse. This regime approaches equilibrium growth conditions under which the equilibrium free energy of formation of the 'c' type phase is great enough to

overcome the kinetic path afforded to 'a' type domains by the growth rate anisotropy and only 'c' type grains nucleate and grow. Note that the 'a' and 'c' surface mobility approach a constant value. A similar trend is seen in the variation of the film orientation with temperature at a constant deposition rate of 0.001. High temperatures are again nucleation limited, and polycrystalline films of 'c' type domains prevail. As the temperature decreases, the growth anisotropy intercedes and 'a' type films become dominant. Note the corresponding crossover in surface mobilities. At very low temperature, the growth anisotropy is overcome by the equilibrium free energy of formation for 'c' type material, and 'c' type grains prevail. Preliminary results for conditions under which 'a' type growth is energetically preferred do not show the 'a' to 'c' to 'a' transformation, as here, 'a' type is both the kinetically and energetically preferred phase.

The films used in these studies were very thin and on the order of 3.2 nm thick. Thus the resulting films tend to be completely homogeneous through thickness which results in the sharp transitions from 'a' to 'c' type films. It is expected that these sharp transitions will "round" out for greater film thicknesses, reflecting substrate retained material of a subordinate orientation type in a given deposition range. In many ways the modified plots of Figures 4a and 4b could then be thought as isothermal and isochronal sections taken through a classical TTT (Time-Temperature-Transformation) where time is replaced by deposition rate and the transformation altered to indicate the degree of 'a' or 'c' type film.

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720