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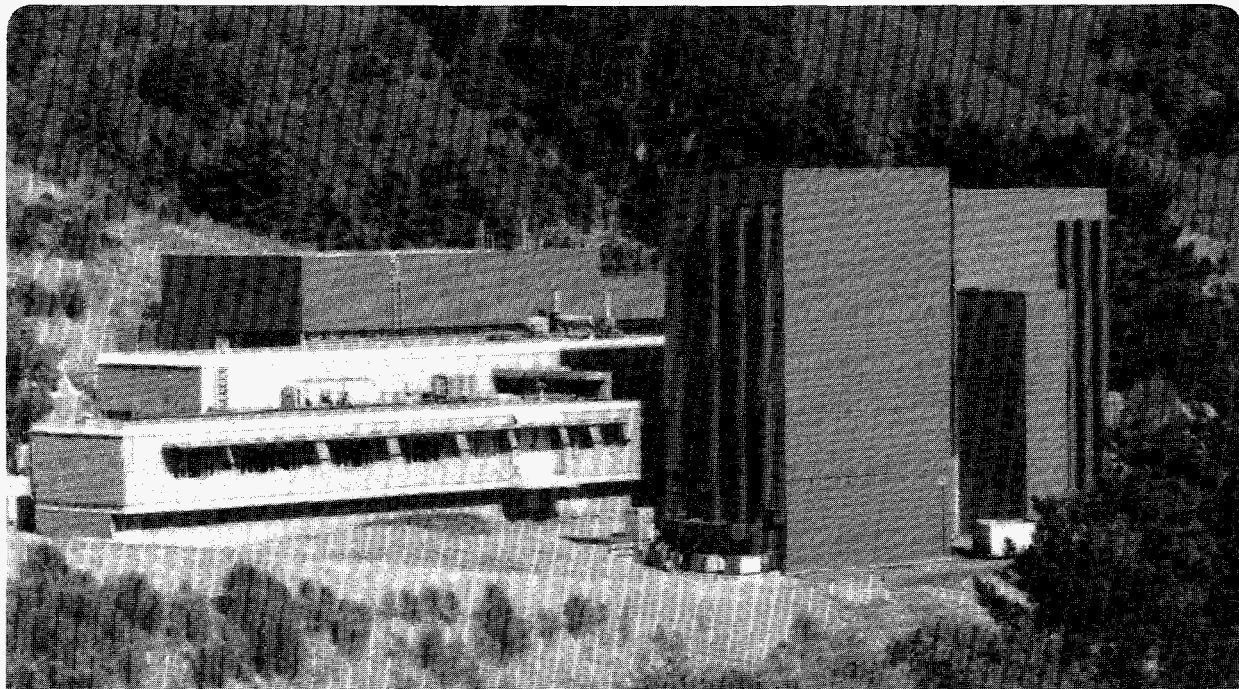
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C.P. Burmester, L.T. Wille, and R. Gronsky

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

Materials Sciences Division
Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720
&
Materials Sciences and Mineral Engineering
University of California
Berkeley, CA 94720

*Florida Atlantic University
Dept. of Physics
Boca Raton, FL 33431

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SIMULATION OF MULTICOMPONENT THIN FILM DEPOSITION AND GROWTH

C. P. BURMESTER[†], L. T. WILLE[‡], AND R. GRONSKY[†]

[†]University of California, Department of Materials Science and Mineral Engineering and Lawrence Berkeley Laboratory, Materials Science Division, Berkeley, CA 94720

[‡]Florida Atlantic University, Department of Physics, Boca Raton, FL 33431

ABSTRACT

Results from a multicomponent Monte Carlo simulation of the deposition and growth of $YBa_2Cu_3O_7$ are presented and discussed. In particular, a detailed examination of the growth modes active during different morphological growth conditions is performed. At higher deposition rates, both [001] and [100] epitaxial variants ('c' and 'a' type growth, respectively) are observed to grow by modes attributed to the classic Volmer-Weber mechanism. At very low deposition rates, the film is observed to grow in a distinct, cyclic, multi-stage process. Small islands of [001] epitaxy nucleate and grow to one unit cell height followed by primarily horizontal growth or "ledge extension" until one unit cell layer has formed. This process then repeats. Simulated RHEED amplitude data from this growth process compares favorably to experimentally obtained data.

INTRODUCTION

Thin film deposition and growth is one of the most widely applied and intensely studied new materials technologies. Applications include semiconducting microelectronic devices, ferroelectric films for memory devices, optical coatings, biomedical implants, and magnetic recording media to touch on just a few. While the technology of applications in thin film science is quite extensive, theoretical understanding of these processes is still quite poor. Development of thin film processes remains system specific guided mainly by experience and empirical rules with the bulk of the existing theory based on continuum capillarity approaches which neglect atomistic details important in the evolution of microstructure and the electromagnetic performance of thin film devices. To compound this issue, many of the most technologically exciting new thin film materials are derived from multicomponent systems.

These theoretical shortcomings stem in part from the complexity of thin film deposition processes.¹ Some of the many possible variables include substrate type, orientation, and defect density, substrate or ambient temperature, deposition technique, source ratios, deposition atmosphere, deposition rate, and post annealing processes. Many of these variables, like temperature and the coefficient of thermal expansion of the substrate, are related in a complex fashion. While the large number of thin film studies are providing insight into the general effects of specific deposition conditions on thin film growth, it is difficult to design an ideal experiment that precisely controls all but one of the many variables to allow investigation of the effect of a particular parameter on film growth. In this, computer simulation can provide the degree of control over "experimental" conditions and the spatial and temporal resolution necessary to complement experimental studies of thin film systems. In what follows, results of a multicomponent Monte Carlo simulation of $YBa_2Cu_3O_7$ are presented.

MODEL AND PREVIOUS FINDINGS

The details of the simulation method used in this study have been published elsewhere.² In brief, simulation particles representing yttrium and barium perovskite units, and a copper-oxygen unit are deposited into a three dimensional cubic lattice with periodic boundary conditions in the x and y directions (in the conventional sense) with the z direction being bounded by the substrate below and a free boundary above. Interactions are a function of particle type and crystallographic direction and act only between nearest neighbors. Three simulation

excitation modes are performed representing deposition, surface diffusion, and bulk annealing. The latter mode acts to attempt a realignment of the deposition particle's "spin" property, a property which specifies the current orientation of its crystal domain.

In previous studies, two distinct epitaxial variants were found to occur. These were individually characterized as an 'a' type, with [100] direction oriented perpendicular to the substrate, and a 'c' type, with [001] direction oriented perpendicular to the substrate. Through a systematic variation of deposition rate and substrate temperature during in-situ deposition, it was observed that transitions between these different growth variants occurred. At constant substrate temperature, very low deposition rates produced films with a 'c' type morphology. Higher deposition rates yielded 'a' type morphology. Increasing the deposition rate further leads to defected 'c' type films and then ultimately to nearly amorphous films. A similar behavior was observed as a function of substrate temperature. Low and high substrate temperatures at a constant deposition rate yielded 'c' type films while an intermediate substrate temperatures yielded a 'a' type morphology. A subsequent investigation³ of the influence of substrate mismatch on film growth suggested that different growth mechanisms were operating and responsible for the distinct morphologies observed. In particular, it was found that increasing "substrate strain" favored the growth of the low deposition rate 'c' morphology over the 'a' type morphology. An interpretation of this in terms of capillarity theory would suggest that the low deposition rate 'c' regime has a growth mechanism with more "island" character than the 'a' type regime. On the surface, such an observation would seem to contradict the general belief that the low deposition rate (low supersaturation) 'c' type films grow via a "layer-by-layer" mechanism. To resolve this apparent contradiction and to better characterize the growth of these morphologies, a detailed investigation of their modes of growth was performed.

RESULTS AND DISCUSSION

There are three generally accepted modes of film growth⁴: "layer" or Frank-van der Merwe (FM) growth, "island" or Volmer-Weber (VW) growth, and "layer-plus-island" or Stranski-Krastanov (SK) growth. In FM growth, a monolayer nucleates on the substrate and extends to cover the surface before a second layer is nucleated on top. This mode of film growth typically prevails at low deposition rate or low surface saturation and high particle mobility as this gives material ample time to migrate to the advancing ledge. In VW growth, material nucleates in small islands and grows both upwards and outwards via overgrowth and ledge extension. Many islands nucleate on the substrate and these grow and coalesce. This mode of growth tends to prevail under high deposition rates or conditions of low mobility (low temperature). Higher deposition rates tend to increase the number of nuclei formed. In SK growth, a few monolayers grow to cover the substrate, as in FM growth, then islands nucleate and grow via the VW mechanism. Such a mechanism operates when substrate conditions favor wetting but either the deposition rate or the surface of the growing material favors island growth.

A common analytical method for discerning which of these classic modes are operating during film growth is to examine the "roughness" or the standard deviation of the film height as a function of time. The roughness, $\Delta\theta$, is given by:

$$\Delta\theta = \sqrt{\theta^2 - \left(\frac{1}{N} \sum_i h_i^2\right)} \quad (1)$$

where θ , the coverage or average film height, is defined by:

$$\theta = \frac{1}{N} \sum_i h_i \quad (2)$$

and N is the number of surface sites. The roughness distinguishes between growth modes in the following fashion. Layer growth leads to a periodic roughness arising from the sequential filling of single layers as is often detected via Reflection High Energy Electron Diffraction (RHEED),

island growth has a linearly increasing roughness, whereas in layer-plus-island growth the first few layers lead to a number of oscillations characteristic of layer growth followed by a linearly increasing value corresponding to island growth.

Roughness plots as a function of time obtained from simulations of the growth of the higher 'a' and 'c' morphological variants revealed, after an initial onset rise attributed to substrate effects, nearly linear increasing values indicative of "island" or VW growth (Figure 1). Roughness data for the low deposition rate variant revealed a drastically different behavior. Here, the roughness was observed to oscillate periodically as is the case with classic "layer" or FM growth. However, the period of the oscillations was found to correspond to the growth of exactly one unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_7$, itself composed of many distinct atomic layers (Figure 2). Detailed examination of this growth mode with the simulation revealed a novel growth behavior. An examination of film cross-sections obtained during growth revealed that small islands of [001] epitaxy would nucleate and grow as islands to one unit cell height (Figure 3). After this, all further growth was observed to be largely constrained to the horizontal direction, via ledge extension, until a complete unit cell layer had formed. This process would then repeat with the nucleation of new [001] islands on the surface of the newly formed layer. The formation of each layer was found to correspond exactly to one oscillation in the roughness plot. The cross-sections of Figure 3 were chosen to correspond with certain roughness values found in Figure 2. In particular, with reference to Figure 2, the first cross-section of Figure 3 was taken just prior to the first roughness maximum at 224 Monte Carlo Steps per Particle (MCSP), the second at the first roughness maximum at 480 MCSP, the third at the first roughness minimum at 1632 MCSP, and the fourth at the second roughness maximum at 2240 MCSP. Similar behavior to that revealed in Figure 2 has been observed via experimental RHEED studies.⁵ These studies have also attributed each oscillation to the growth of one unit cell height. By contrast, the 'a' type films grow by a standard "island" mechanism (Figure 4). Cross-sections reveal that small islands nucleate and continue to expand both horizontally and vertically. These cross-sections were taken at 800, 1600, 2400, and 3200 MCSP, respectively. In all cross-sections, lines run along the [100] directions ('a' or 'b') and large open circles indicate barium atoms, large filled circles yttrium atoms, and small filled circles copper atoms. Oxygen positions are not represented for graphical clarity. The cross-sections reveal a much high density of layer stacking disorder and defects, especially near the surface of the growing film and in the higher deposition rate variant. In the latter case, this defect density is greater than encountered experimentally and is likely due to the simulation model limitation of only nearest neighbor pairwise interactions. While longer ranged interactions would likely remedy this inconsistency, the overall morphological film growth characteristics of this system are well described, as detailed elsewhere.²

A notable feature of the low deposition rate roughness plot is that the first oscillation is anomalously large while the subsequent oscillations are equal in amplitude. This effect is attributed to the influence of the substrate in the simulation in the following fashion. The substrate in this simulation interacts with all deposition particles equally. Thus, a nucleating island with [001] orientation can grow on the substrate equally well beginning with a yttrium, barium, or copper layer. As these distinct islands grow horizontally to cover the substrate, they come into contact forming antiphase boundaries and a competition between domains ensues until one domain type grows at the expense of the others to cover the substrate. This competition between domains in the first layer is postulated to be the cause of the anomalously large amplitude of the first roughness oscillation. Subsequent layers grow by homo-epitaxy so such a competition is either not expected or is much smaller in magnitude. This effect can be observed directly in the first two cross-sections of low deposition rate 'c' growth depicted in Figure 3. The first few nuclei form with either copper or yttrium layer on the substrate. By the third cross-section, the nucleus with yttrium as its first layer has grown to cover the substrate and further layers grow in accordance with this layering sequence. In experimental RHEED studies of this system, it is often observed that the first RHEED oscillation is anomalously low (due to scattering as a result of a large roughness), entirely analogous to what is observed by simulation here. Indeed, a similar effect can be expected as the substrate material provides a distinct surface from the surface of the deposited material.

What is distinctly novel about the growth mode observed for the low deposition rate 'c' variant is that while it macroscopically behaves as a "layer" or FM growth mechanism, in its

initial stages, the mode has "island" or VW mechanism characteristics. This dual effect arises from the fact that each growth layer ultimately consists of one unit cell thickness, itself composed of many atomic layers, which initially nucleate as small sub-unit cell thickness islands which then rapidly grow in VW fashion to unit cell height, presumably to satisfy chemical bonding and electro-neutrality constraints present in this multicomponent oxide system. The dual driving forces of adsorption of atomic or molecular deposition species and the chemical and electrical stability of the unit cell ordering appear to act in opposition to lead to a cyclic, multi-stage growth mechanism of alternating "island" and "layer" character. What distinguishes this mechanism from classical "layer" or FM growth is that the mechanism responds to external stresses as does "island" growth, even though its macroscopic signature is that of "layer" growth, as borne out by the roughness oscillations and experimental RHEED studies. This interpretation is supported by earlier simulations studies of the effects of substrate strain on film growth morphologies.³ Increasing substrate strain was found to favor the growth of the low deposition rate 'c' variant over the 'a' variant. Applying a capillarity theory interpretation, this can only be explained if the 'c' type variant has a greater "island" growth character than the 'a' type variant, which would seem to rule out classic FM growth for the low deposition rate 'c' variant. However, the cyclic, multi-stage growth mechanism reported here behaves in its initial stages as does "island" growth, yielding a consistent interpretation of both the observed roughness oscillations and substrate strain response behavior.

In conclusion, a simulation study is performed to ascertain the growth modes responsible for the various 'c' and 'a' type morphological variants arising as a function of deposition rate observed both in this simulation and in experimental studies. Surface roughness studies indicate that the high and medium deposition rate 'c' and 'a' type variants grow via an "island" or Volmer-Weber mechanism. The very low deposition rate 'c' variant is observed to grow via a novel cyclic, multi-stage process yielding an oscillating surface roughness as a function of time. In this mechanism, small islands of [001] epitaxy nucleate and grow to one unit cell height followed by primarily horizontal growth until one unit cell layer has formed. This process then begins anew with the nucleation of [001] islands atop the newly formed layer. This mechanism yields a consistent interpretation of seemingly contradictory results provided by surface roughness and substrate strain response studies. While this novel growth mechanism has been observed in a simulation of the $YBa_2Cu_3O_7$ system, it is expected to be a viable growth mechanism in other multicomponent layered oxide systems at low deposition rates.

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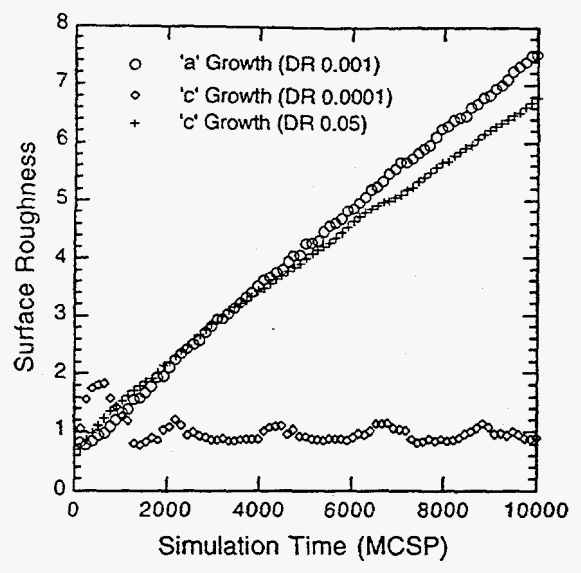


Figure 1: Surface roughness as a function of simulation time for the three distinct growth regimes. The linearly increasing roughness for the higher deposition rate 'c' and 'a' regimes indicates an "island" growth mechanism while the oscillating roughness for the low deposition rate 'c' regime indicates a "layer" type growth mechanism (DR = Deposition Rate).

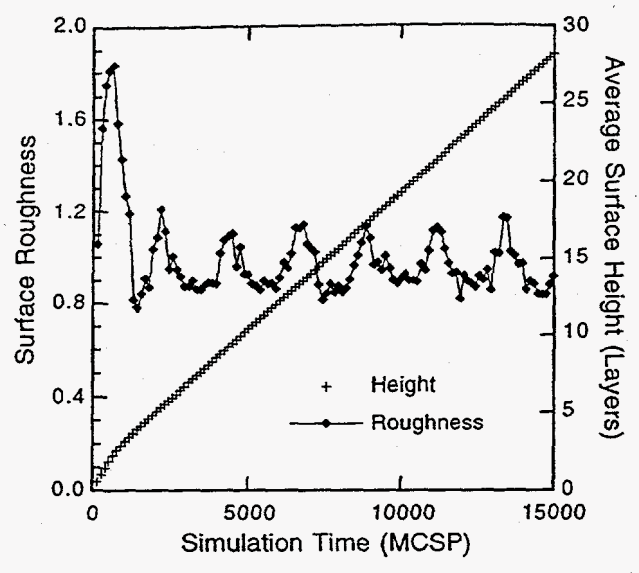


Figure 2: Surface roughness and average surface height as a function of simulation time for the low deposition rate 'c' regime. Distinct growth oscillations are apparent. Each oscillation corresponds to four simulation layers or one unit cell thickness.

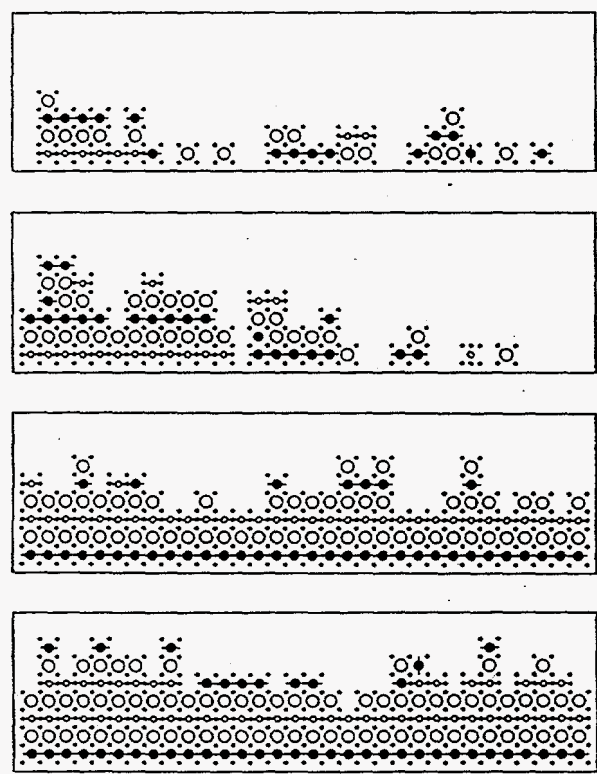


Figure 3: Cross-sections as a function of time for the first few unit cell layers in the low deposition rate 'c' regime. The film grows by a multi-stage "layer" mechanism consisting of unit cell layers.

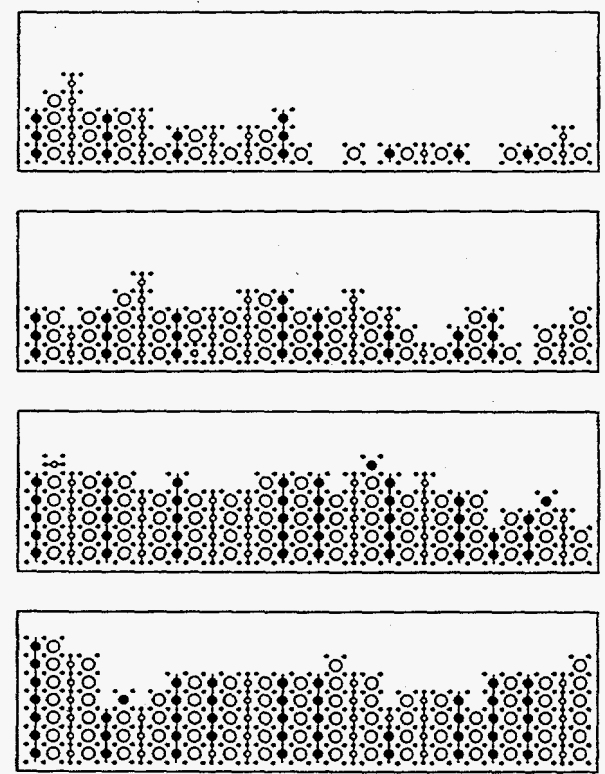


Figure 4: Cross-sections as a function of time for the first few unit cells of growth in the 'a' regime. The film grows via an "island" mechanism.

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