DEFECT-MEDIATED GROWTH OF $YBa_2Cu_3O_{7-\delta}$ FILMS

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ABSTRACT

The evolution of the surface microstructure of sputtered *c*-axis oriented epitaxial $YBa_2Cu_3O_{7-\delta}$ films has been monitored by scanning tunneling microscopy (STM). The results indicate that growth is dominated by the incorporation of depositing species at defect sites. These defect sites, which provide energetically favorable positions for accommodating the arriving species, are at ledges—either along growth spirals emanating from screw dislocations, or due to the closely spaced surface steps arising from the macroscopic tilt of the substrate. If the substrate is misoriented sufficiently, the depositing species may diffuse to and be accommodated by these surface steps, without the supersaturation on the terraces attaining a high enough level for two-dimensional nucleation to occur. Under these conditions, growth occurs by step propagation. Otherwise, a high density of screw dislocations ($\approx 10^9$ cm^{-2}) is nucleated during the initial stages of growth, which provides a continual supply of ledge incorporation sites in the vicinity of the depositing species. The surface evolution reported appears to be an intrinsic feature of *c*-axis oriented $YBa_2Cu_3O_{7-\delta}$ films for a wide range of growth conditions, irrespective of the substrate material or vapor phase deposition method.

INTRODUCTION

Vapor phase deposition techniques have achieved immense success in preparing epitaxial high temperature superconductor thin films with electrical properties superior to those made by bulk synthesis techniques. Such high quality films are produced routinely by a variety of vapor phase deposition methods. Interestingly, these films contain numerous defects, frequently including a high density of screw dislocations (10^8-10^{10} cm^{-2}), which have been observed in *c*-axis oriented $YBa_2Cu_3O_{7-\delta}$ films grown by virtually all vapor deposition growth methods on all of the common substrate materials. For example, high densities of screw dislocations have been observed in films grown by sputtering [1-7], pulsed laser deposition [6-10], thermal evaporation [11], chemical vapor deposition (CVD) [7], and molecular beam epitaxy (MBE) [12,13] on $SrTiO_3$ {100} [1,2,5-7,12,13], MgO {100} [2,3,6,7,11,13], $LaAlO_3$ {100} [9], yttria-stabilized ZrO_2 {100} [8], $NdGaO_3$ (001) [4,13], and Mg_2TiO_4 {100} [10]. These screw dislocations not only may be strong vortex pinning sites which enhance the critical current densities of the thin films [14], but also reveal the film growth mechanism [6,15]. Despite the widely varying growth conditions which accompany these different growth methods, the specific conditions used by different research groups, and the range of lattice match, crystal structure, substrate perfection, and surface preparation of these substrates, definite similarities exist in the observed film surface morphologies. These similarities may be readily explained by invoking a common growth mechanism, which will be briefly described here and accounts for the observed microstructure. The present discussion is limited to *c*-axis oriented $YBa_2Cu_3O_{7-\delta}$ films in which the constituent species are co-deposited; detailed studies on films grown by sequential deposition methods are needed to ascertain how such growth conditions impact the film growth process. Efforts to understand the growth mechanism of oxide superconductor films have substantially profited from STM and AFM images of film surfaces; it was these techniques which first detected the presence of numerous screw dislocations in oxide superconductor films [1,2].

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GROWTH MECHANISM

The presence of a high density of growth spirals emanating from screw dislocations in *c*-axis oriented $YBa_2Cu_3O_{7-\delta}$ films [1-13,15] indicates that film growth takes place by accommodating species along the spiral shaped step which emanates from each screw dislocation. Surface steps are energetically favorable attachment sites [16]. As growth proceeds, the growth spirals rotate around the screw dislocations at their centers, ascending one layer higher with each rotation. In this manner screw dislocations produce self-perpetuating (spiral-shaped) surface steps. This well-know growth mechanism, first proposed by Frank [17], has been observed for the growth of other *c*-axis oriented layered micaceous materials, and for the growth of the basal plane of many hexagonal materials [18-22].

The growth process of *c*-axis oriented $YBa_2Cu_3O_{7-\delta}$ films may be generally described as ledge growth, emphasizing the energetic preference of the depositing species to attach to existing ledges (step edges), which propagate laterally across the substrate surface. This process and the various types of ledge sites available for attachment are schematically shown in Fig. 1. As the spacing between existing ledges on the growth surface is increased, the concentration of adatoms on the terraces is also increased. For sufficiently wide terraces the supersaturation at positions far from the ledges becomes high enough for two-dimensional nucleation to occur. However, such nucleation events are unlikely when the depositing species are in the vicinity of a ledge. This is because the energy barrier to two-dimensional nucleation is large enough that the species statistically are more likely to have attached to the existing ledge long before they reach a sufficient supersaturation to nucleate a new layer. Thus, it is inferred that the presence of defect sites dramatically affects the crystal growth process.

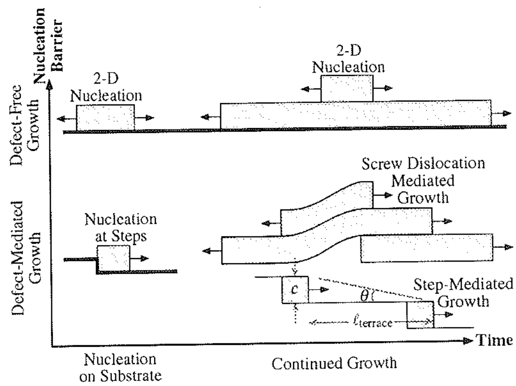

FIGURE 1: Schematic representation of the ledge growth process inferred from the growth of *c*-axis oriented $YBa_2Cu_3O_{7-\delta}$ films. The high nucleation barrier to forming a new layer by two-dimensional nucleation requires a high supersaturation to be reached for such nucleation to take place. The presence of more energetically favorable ledge attachment sites in the vicinity of the depositing species (e.g., emanating from screw dislocations or those present on vicinal substrates) accommodates the depositing species and reduces the supersaturation such that after the initial stages of growth, two-dimensional nucleation is rare.

At the initiation of growth, the only available ledge sites on a perfect substrate are surface steps. Indeed TEM studies show that the initial nucleation occurs predominantly there [23]. If the substrate is sufficiently well oriented and the substrate temperature low enough that the supersaturation on the terrace can reach the level required for two-dimensional nucleation, growth will take place by the nucleation of new layers (two-dimensional nucleation) in regions far from ledges. However, if a sufficient density of screw dislocations were to be generated (possible mechanisms for which are described below), an endless supply of energetically favorable ledge attachment sites would be available to accommodate the depositing species. Since the observed surface morphologies indicate the presence of high densities of screw dislocations in $YBa_2Cu_3O_{7-\delta}$ films grown on well oriented substrates, screw dislocation generation clearly has taken place. STM studies [1,6] have revealed the presence of a high density of screw dislocations in films as thin as ≈120 Å thick, indicating that the screw dislocations are generated in the initial stages of film growth.

When slightly misoriented from (100), the microscopic surface structure of commonly used substrates consists of a sequence of steps separating (100) terraces. These surface steps are favorable sites for nucleation and subsequent growth [16]. Although the substrate step height does not match the layer height of $YBa_2Cu_3O_{7-\delta}$, a sequence of steps develops, separating (001) $YBa_2Cu_3O_{7-\delta}$ terraces and accommodating the macroscopic tilt of the substrate. As growth proceeds by the incorporation of the depositing species at these steps, the steps propagate across the film surface. The amount of substrate tilt necessary to achieve growth mainly by this step propagation growth mechanism is presumably that which causes the steps to be spaced sufficiently close together that the depositing species diffuse to and are accommodated by the existing ledges without reaching a supersaturation on the terrace sufficient for two-dimensional nucleation [24]. Experimentally, a cross-over from screw dislocation mediated growth to step propagation has been observed on vicinal $SrTiO_3$ (100) surfaces, and the amount of tilt necessary decreases as the growth temperature is increased [6]. This cross-over is shown in Fig. 2 for the sputtered growth of $YBa_2Cu_3O_{7-\delta}$ on $SrTiO_3$ at a substrate block temperature of 750 °C [6]. Under these growth conditions, the transition occurs at about $\theta_c \approx 2°$, which implies an average terrace spacing of about 30 nm. Growth on less vicinal substrates under the same growth conditions results in a comparable terrace spacing (≈20 nm [6]) between turns of the growth spirals, as is to be expected for this analogous defect-mediated ledge growth process. With additional data (e.g., the surface free energy and the concentration of adatoms at the ledges) the surface diffusion coefficient may be calculated from this cross-over terrace spacing. However, this spacing alone is insufficient to make such a determination [24]. The influence of substrate orientation on the film growth mechanism explains the apparently disparate results of several studies (in which substrate misorientations were not reported) where nominally identical growth conditions yielded drastically different growth morphologies [3,5].

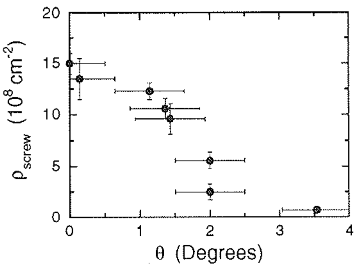

FIGURE 2: Screw dislocation density (ρ_{screw}) as a function of substrate misorientation angle (θ) for sputtered 1000-1500 Å thick $YBa_2Cu_3O_{7-\delta}$ films grown at $T_{sub} \approx 750$ °C and a growth rate of 0.5-1.8 Å/sec on nominally (100) oriented $SrTiO_3$ substrates [6].

Reflection high energy electron diffraction (RHEED) intensity oscillations are not expected to occur for growth occurring by the addition of species to established growth spirals or to a propagating sequence of surface steps, since the surface step density is essentially time independent for these growth modes. Indeed, the observation of RHEED intensity oscillations has only been reported [25,26] to occur during the initial stages of growth (for thickness ≲200 Å for $YBa_2Cu_3O_{7-\delta}$ films) on bare substrates, indicative of the time necessary for a steady state surface step density to become established. On thicker films, no RHEED intensity oscillations are seen, even if the growth is briefly interrupted [25,26].

NUCLEATION OF SCREW DISLOCATIONS

An important but so far unresolved issue is the mechanism of nucleation of the screw dislocations. Two likely mechanisms, which have been documented for the growth of other layered micaceous materials [19-22], are (1) the coalescence of two separate growth fronts having vertically offset and inclined surfaces with respect to each other, and (2) the recombination of two branches of a single growth front which became offset in layer height from each other during growth. The ability of $YBa_2Cu_3O_{7-\delta}$ to flow over irregularities [27] (which can lead to offsets in layer height between coalescing growth fronts and thus the nucleation of screw dislocations) is facilitated by the ledge growth mechanism. The first mechanism of screw dislocation nucleation is likely to occur during the coalescence of the initial nuclei that form on the substrate surface. Obstacles leading to the second mechanism of screw dislocation nucleation may include impurity particles or even steps on the substrate surface. For example, nanometer-size Y_2O_3 precipitates with concentrations over two orders of magnitude higher than the surface screw dislocation density have been identified in $YBa_2Cu_3O_{7-\delta}$ films [28]. These precipitates are of appropriate size and density to give rise to the "holes" observed in STM images [1,6] and to precipitates detected as hillocks in AFM studies [29], which have been observed at positions around which the growth fronts have developed branches. In-plane alignment of the coalescing nuclei is necessary for the first nucleation mechanism to occur, and this is made possible by the epitaxial alignment of the individual nuclei to the underlying substrate. TEM and STM images of ultra-thin $YBa_2Cu_3O_{7-\delta}$ films contain features suggestive of screw dislocation nucleation, consistent with these two nucleation mechanisms [30,31].

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