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Microdiffraction Study of Epitaxial Growth and Lattice Tilts in Oxide Films on Polycrystalline Metal Substrates

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Introduction

Texture, the preference for a particular crystallographic orientation in polycrystalline materials, plays an important role in controlling such diverse materials properties as corrosion resistance, recording density in magnetic media and electrical transport in superconductors [1]. Without texture, polycrystalline oxide superconductors contain many high-angle, weak-linked grain boundaries which reduce critical current densities by several orders of magnitude [2]. One approach for inducing texture in oxide superconductors has been the epitaxial growth of films on rolling-assisted biaxially-textured substrates (RABiTS) [3]. In this approach, rolled Ni foils are recrystallized under conditions that lead to a high degree of biaxial $\{001\}\langle 100\rangle$ cube texture. Subsequent deposition of epitaxial oxide buffer layers (typically CeO₂ and YSZ as chemical barriers) and superconducting YBCO preserves the lattice alignment, eliminating high-angle boundaries and enabling high critical current densities, $J_c > 10^6/\text{cm}^2$. Conventional x-ray diffraction using ω - and ϕ - scans typically shows macroscopic biaxial texture to within $\sim 5^\circ$ - 10° FWHM for all layers, but does not describe the *local* microstructural features that control the materials properties. Understanding and controlling the *local* texture and microstructural evolution of processes associated with heteroepitaxial growth, differential thermal contraction and cracking remain significant challenges in this complex system [4], as well as in many other technologically important thin-film applications.

Methods and Materials

We have studied the *local* crystallographic orientation and strain in epitaxial CeO₂ films grown by pulsed laser deposition (PLD) on Ni substrates using recently-developed Laue x-ray microbeam diffraction techniques [5-8]. In these studies, white undulator radiation is focused to submicron diameter using a crossed-pair of elliptical Kirkpatrick-Baez mirrors. The polychromatic beam penetrates both the film and the substrate and simultaneously gives rise to CeO₂ and Ni Laue diffraction patterns which are measured by a CCD detector. Quantitative analysis of the patterns yields the local lattice orientation (resolution $\sim 0.01^\circ$) and deviatoric strain tensor (resolution $\sim 10^{-4}$) for each layer. The patterns reveal that the cubic fluorite CeO₂ and fcc Ni principal in-plane crystallographic axes are related by the expected 45° rotation, corresponding to $\sim 9\%$ lattice mismatch.

However, they also show that the out-of-plane film and substrate (001) plane normals are not exactly aligned [5]. Instead, we observe a small crystallographic tilt of the oxide lattice relative to the Ni lattice, typically with the film [001] pole tilting towards alignment with the sample surface normal. Note that microbeam patterns at different locations on a single sample provide measurements from a large number of grains with different vicinal surfaces grown under identical conditions. Previous investigations of epitaxy on off-axis surfaces required that a new sample be grown on a large single-crystal for each miscut angle. Use of microbeam diffraction and a textured substrate eliminate this limitation and, in effect, enables a combinatorial approach to the measurement of heteroepitaxial growth.

To systematically investigate the heteroepitaxial tilting mechanism and its dependence on kinetics, a set of CeO₂ films on Ni substrates were grown at four different temperatures over the range $450^\circ\text{C} - 785^\circ\text{C}$ under otherwise identical PLD conditions [9]. Here, all CeO₂ films were $0.5\ \mu\text{m}$ thick and were deposited in an initially reducing atmosphere (4% H₂/Ar, 0.1 Torr) onto $50\ \mu\text{m}$ thick textured Ni (mosaic $\sim 8^\circ$ FWHM) foils. X-ray microdiffraction Laue patterns ($0.7\ \mu\text{m}$ diameter beam) were measured at many positions within randomly selected grains on each of the four samples. Automated software was then used to index and analyze the Laue patterns, yielding orientation matrices and deviatoric strain tensors from both the film and the substrate. In addition, large-area orientation maps from both the film and the substrate in a RABiTS sample were obtained by scanning the microbeam over a $0.7 \times 0.7\ \text{mm}^2$ area with $8\ \mu\text{m}$ step size.

Results

CeO₂ films grown at different deposition temperatures exhibited significant microstructural differences [5]. At high growth temperatures (600 - 800°C), the film and substrate (001) poles were not aligned. Instead the film (001) planes tilted towards the surface normal, and importantly, the tilts were not statistical; they were *locally* determined by the substrate orientation. The magnitude of the lattice tilts increased linearly as the local substrate surface miscut angle increased. Tilts greater than 4° were measured for large miscut angles. No in-plane components to the crystallographic tilts were observed; i.e. the film $\langle 110\rangle$ and substrate $\langle 100\rangle$ axes were aligned in-plane. In contrast, at the lowest growth temperature

(450°C), lattice directions in the film were epitaxially aligned in all three dimensions within 0.5° with those in the Ni substrate.

These qualitative differences in microstructure associated with deposition temperatures can be understood in terms of how changes in the kinetic energy of deposited atoms can result in different growth modes [5]. At higher temperatures, the deposited material has sufficient surface mobility that growth proceeds by step-ledge propagation as shown schematically in Figure 1a. At the lower growth temperature, surface mobility is kinetically suppressed so that isolated islands are nucleated initially on the flat surface terraces (Figure 1b).

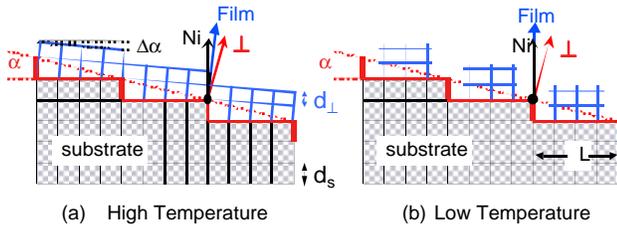


FIG. 1. Schematic of epitaxial growth modes for oxide films on miscut Ni surfaces. 1a. Growth by step-ledge propagation with lattice tilts at high substrate temperatures. 1b. Film deposition begins with island formation on flat terraces at low substrate temperatures.

Detailed models of epitaxial growth can be derived based on these two different growth modes. During high-temperature ledge growth, thin CeO₂ (001) films are tetragonally strained to match the out-of-plane substrate lattice spacing, d_s , at the surface ledge, but relaxes to the unstrained film value, d_f , across each terrace distance, L . This model predicts that the film [001] will tilt toward the surface normal for $d_f < d_s$, in agreement with the linear relation measured for CeO₂ films. Microdiffraction measurements for epitaxial yttria-stabilized zirconia (YSZ) and LaMnO₃ films on textured Ni substrates were also obtained and were in qualitative agreement with predictions from this model. During low-temperature deposition, nucleation and growth occur on the flat terraces independent of surface steps; thus the crystallographic orientation of the substrate is preserved in the epitaxial film.

Discussion

The crystallographic tilts described in these studies are of significant practical importance as the misorientation angles between neighboring grains strongly impact the critical current transport in coated superconductor applications. Since the critical current density of a grain boundary decreases exponentially with the misorientation angle, maintaining a percolative path with boundaries $< \sim 5^\circ$ throughout a large region is considered an important criterion for performance. Figure 2 shows color-coded orientation maps for both the Ni substrate and the oxide

buffer generated using x-ray microdiffraction Laue measurements. Black lines designate “blocking” boundaries between adjacent pixels misoriented by a total angle greater than 5°. Each color indicates a contiguous region connected by paths with misorientations less than 5°. For the Ni substrate, low-angle connectivity extends across the sample in the horizontal, but not the vertical direction. In contrast, enhanced texture in the film due to crystallographic tilts results in larger connected regions

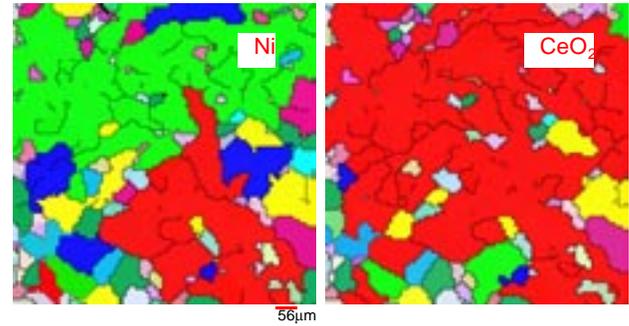


FIG. 2. Orientation maps produced by x-ray microdiffraction. Black lines indicate boundaries between pixels where the total misorientation is greater than 5°. Each colored area shows a percolative region connected by boundaries of less than 5°.

and percolation in both the horizontal and vertical directions.

The tilt mechanisms studied here should be relevant to many oxide/metal systems, including thermal barrier coatings, solar cells, corrosion, and interfaces in electronic devices. Thus, the benefits of intentionally-enhanced texture should be achievable for many coated materials. More generally, the results reported here illustrate how the previously missing ability to obtain *local* structure, orientation and strain information by x-ray microdiffraction will provide unique fundamental information for a wide range of materials disciplines.

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