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 diverse materials properties, such 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}<100> cube texture. Subsequent deposition of epitaxial oxide buffer layers (typically CeO_2 and YSZ as chemical barriers) and superconducting YBCO preserves the lattice alignment, eliminating high-angle boundaries and enabling high critical current densities (J_c of $>10^6$/cm^2). Conventional x-ray diffraction using ω- and ϕ-scans typically shows macroscopic biaxial texture to within ~5°to 10° full width at half maximum (FWHM) for all layers, but it 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 CeO_2 films grown by pulsed laser deposition (PLD) on Ni substrates by using recently developed Laue x-ray microbeam diffraction techniques [5-8]. In these studies, white undulator radiation is focused to submicron diameter by using a crossed pair of elliptical Kirkpatrick-Baez mirrors. The polychromatic beam penetrates both the film and the substrate and simultaneously gives rise to CeO_2 and Ni Laue diffraction patterns, which are measured by a charge-coupled device (CCD) detector. Quantitative analysis of the patterns yields the local lattice orientation (resolution ~0.01°) and deviatoric strain tensor (resolution ~10^{-4}) for each layer. The patterns reveal that the cubic fluorite CeO_2 and fcc Ni principal in-plane crystallographic axes are related by the expected 45° rotation, corresponding to ~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 toward 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 eliminates 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 CeO_2 films on Ni substrates was grown at four different temperatures over the range 450°–785°C under otherwise identical PLD conditions [9]. Here, all CeO_2 films were 0.5-µm thick and deposited in an initially reducing atmosphere (4% H_2/Ar, 0.1 Torr) onto 50-µm-thick textured Ni (mosaic ~8° FWHM) foils. X-ray microdiffraction Laue patterns (0.7-µm-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 × 0.7 mm^2 area with an 8-µ step size.

Results

CeO_2 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 toward the surface normal, and more 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 <110> and substrate <100> 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 Fig. 1(a). At the lower growth temperature, surface mobility is kinetically suppressed so that isolated islands are nucleated initially on the flat surface terraces [Fig. 1(b)].

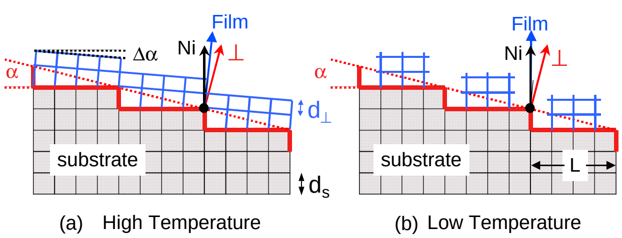

FIG. 1. Schematic of epitaxial growth modes for oxide films on miscut Ni surfaces. (a) Growth by step-ledge propagation with lattice tilts at high substrate temperatures. (b) Film deposition begins with island formation on flat terraces at low substrate temperatures. © 2003 by The International Union of Crystallography, http://journals.iucr.org/.

Detailed models of epitaxial growth can be derived on the basis of these two different growth modes. During high-temperature ledge growth, thin CeO_2 (001) films are tetragonally strained to match the out-of-plane substrate lattice spacing d_s at the surface ledge but relax 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 CeO_2 films. Microdiffraction measurements for epitaxial yttria-stabilized zirconia (YSZ) and $LaMnO_3$ 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 of less than ~5° 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 by 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 and percolation in both the horizontal and vertical directions.

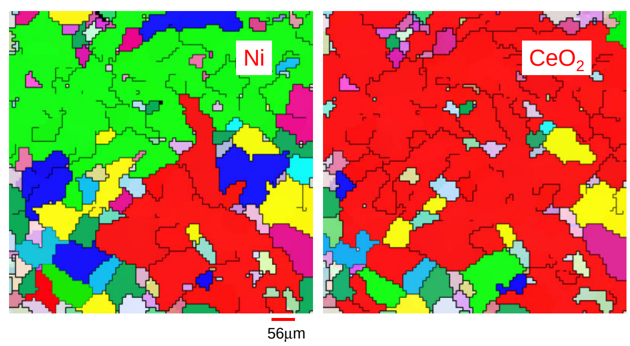

FIG. 2. Orientation maps produced by x-ray microdiffraction. Black lines indicate boundaries between pixels where the total misorientation is greater than 5°. Each colored area shows a percolative region connected by boundaries of less than 5°. © 2003 by The International Union of Crystallography, http://journals.iucr.org/.

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 on 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.

Acknowledgments

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References

[1] U.F. Kocks, C.N. Tomé, and H.-R. Wenk, *Texture and Anisotropy, Preferred Orientations in Polycrystals and Their Effect on Materials Properties*. (Cambridge University Press, Cambridge, United Kingdom, 1998).

[2] D. Larbalestier, A. Gurevich, D.M. Feldmann, and A. Polyanskii, Nature **414**, 368-377 (2001).

[3] D.P. Norton, A. Goyal, J.D. Budai, D. Christen, D. Kroeger, E.D. Specht, Q. He, B. Saffian, M. Paranthaman, C. Klabunde, D. Lee, B. Sales, and F. List, Science **274**, 755-757 (1996).

[4] D.P. Norton et al., Mater. Sci. & Eng. B **56**, 86-94 (1998).

[5] J.D. Budai, W. Yang, N. Tamura, J.-S. Chung, J.Z. Tischler, B.C. Larson, G.E. Ice, C. Park, and D.P. Norton, Nat. Mater. **2**, 487-492 (2003).

[6] J.-S. Chung and G.E. Ice, J. Appl. Phys. **86**, 5249-255 (1999).

[7] N. Tamura et al., App. Phys. Lett. **80**, 3724-726 (2002).

[8] B.C. Larson, W. Yang, G.E. Ice, J.D. Budai, and J.Z. Tischler, Nature **415**, 887-890 (2002).

[9] C. Park, D.P. Norton, J.D. Budai, D.K. Christen, D. Verebelyi, R. Feenstra, D.F. Lee, A. Goyal, D.M. Kroeger, and M. Paranthaman, Appl. Phys. Lett. **73**, 1904-1906 (1998).