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Surface-energy-anisotropy-induced orientation effects on Rayleigh instabilities in sapphire

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Abstract

Arrays of controlled-geometry, semi-infinite pore channels of systematically varied crystallographic orientation were introduced into undoped **m**-plane $(1\,0\,\bar{1}\,0)$ sapphire substrates using microfabrication techniques and ion-beam etching and subsequently internalized by solid-state diffusion bonding. A series of anneals at 1700 °C caused the breakup of these channels into discrete pores via Rayleigh instabilities. In all cases, channels broke up with a characteristic wavelength larger than that expected for a material with isotropic surface energy, reflecting stabilization effects due to surface-energy anisotropy. The breakup wavelength and the time required for complete breakup varied significantly with channel orientation. For most orientations, the instability wavelength for channels of radius R was in the range of $13.2R$–$25R$, and complete breakup occurred within 2–10 h. To first order, the anneal times for complete breakup scale with the square of the breakup wavelength. Channels oriented along a $\langle 1\,1\,\bar{2}\,0\rangle$ direction had a wavelength of $\approx 139R$, and required 468 h for complete breakup. Cross-sectional analysis of channels oriented along a $\langle 1\,1\,\bar{2}\,0\rangle$ direction showed the channel to be completely bounded by stable **c**$(0\,0\,0\,1)$, **r**$\{\bar{1}\,0\,1\,2\}$, and **s**$\{1\,0\,\bar{1}\,1\}$ facets.

Keywords: Aluminum oxide; Lithography; Single crystal surfaces; Surface energy (anisotropy); Rayleigh instabilities; Surface waves–capillary waves; Surface structure, morphology, roughness and topography; Faceting

1. Introduction

Capillary phenomena play an important role in the processing and use of a wide range of materials. Dendritic solidification, sintering of powder compacts, coarsening of catalytic supports, instability of pore networks, diffusive healing of cracks, and the morphologic instability of multilayers, thin films, fibers in composites, and aligned rods in directionally solidified eutectics are examples of processes and situations in which capillarity drives microstructural changes that can either enhance or degrade material performance.

The instability of high-aspect-ratio phases such as fluid jets, wires and rods is among the best known of these phenomena, with the initial stability criterion developed by Plateau in 1856 [1], and the first kinetic analysis by Rayleigh in 1879 [2]. Initially continuous cylindrical fluid jets are prone to the development and growth of periodic axial oscillations in their radius that lead to their breakup into a string of isolated droplets with a characteristic size and spacing. Nichols and Mullins [3,4] extended the modeling of Rayleigh instabilities to solids in the 1960s. Solid rods and cylindrical cavities within solids were predicted to evolve into strings of particles or voids with a size and spacing sensitive to the mass transport mechanism dominating the morphologic evolution. The ability to identify the dominant transport mechanism from the spatial characteristics and to estimate the relevant diffusivity from the temporal characteristics allowed for tracerless measurements of transport coefficients in a wide range of systems.

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The analyses of Nichols and Mullins assume an orientation-independent, isotropic specific surface energy. In crystalline solids the specific surface energy often varies with orientation. As a result, equilibrium shapes, rather than being spheres, can be completely or partially facetted, and some unstable high-energy surface orientations can be absent from the equilibrium or Wulff shape [5,6]. The specific energies of stable surfaces generally do not vary significantly in a given material, with variations typically on the order of $\pm 10-20\%$ of the mean surface energy. However, it is not the variation in surface energy per se that matters, but the second derivative of the surface energy with orientation that is critical in dictating the perturbation energetics and kinetically dominant wavelengths [7]. Local surface-energy minima that can stabilize specific crystal facets can also have an enormous stabilizing effect on nonequilibrium morphologies. Thus, in contrast to the behavior of isotropic materials, in which the dominant perturbation wavelength is a well-defined multiple of the rod radius, in materials with varying surface energies the details of the surface-energy anisotropy (SEA) can vary with the crystallographic orientation of the surfaces and lead to a broad spectrum of evolution behavior within a given material. This presents both processing opportunities and challenges. SEA-induced destabilization may provide opportunities for disruption of continuous phases into finer-scale discrete particles. At the other extreme, every tenfold decrease in the size of a cylindrical fiber or rod can decrease the time required for breakup by a factor of as much as 10^4 (when instability is surface-diffusion or interfacial-diffusion controlled) [3,4,8]. Thus, using SEA to stabilize desired nonequilibrium geometries of fine scale structures may become an appealing and perhaps even necessary option.

An extensive program of research spanning two decades has focused on quantifying the SEA of both undoped and doped sapphire (single crystal Al_2O_3) through determinations of the Wulff shape [9–12], and on quantifying the effects of SEA on the morphological evolution of internal voids [9,13–25]. The experimental approach has exploited lithographic processing to produce cavities of controlled geometry in the surfaces of sapphire substrates of known orientation and chemistry. These defects are subsequently internalized by solid-state diffusion bonding [13]. This approach affords a high level of control over the defect geometry, the crystallography of the bounding surfaces, and the chemistry of the enclosing sapphire, the ability to reproduce a structure, and the potential to vary the geometry, crystallography and chemistry independently and systematically. The present paper describes the instability of high-aspect-ratio pore channels etched into an unstable high-energy plane of undoped sapphire, the $\mathbf{m}(10\bar{1}0)$ plane, and compares the evolution behavior at 1700 °C to that obtained in prior work for channels etched into a stable low-energy plane, the $\mathbf{c}(0001)$ plane, that is part of the Wulff shape of sapphire [23]. The results illustrate the broad spectrum of behaviors that can arise, and identifies opportunities for effective SEA-induced stabilization.

2. Background

2.1. Modeling Rayleigh instabilities in isotropic systems

Historically, treatments of the morphologic instability of continuous phases focused on infinite cylinders of radius R with isotropic specific surface energy γ_s, in which perturbations of infinitesimal amplitude α_0 and wavelength λ are assumed to pre-exist [1,2]. Two characteristic quantities emerge from such analyses. The first is a thermodynamic lower limit on the wavelength of growing perturbations, λ_{min}, which is independent of the mass-transport mechanism. Perturbations with $\lambda < \lambda_{min} = 2\pi R$ are unstable and decay. Growth of an infinitesimal-amplitude perturbation with $\lambda > \lambda_{min}$ reduces the interfacial area and thus energy per unit length or volume of the rod. Continued amplitude growth ultimately causes breakup of the continuous phase into strings of discrete particles or pores. The second characteristic quantity, λ_{max}, defines the expected spacing of these particles or pores by assessing the relationship between λ and amplitude growth rate. Perturbations of wavelength λ_{max} increase amplitude most rapidly, and therefore are expected to control the ultimate spacing. For a given transport mechanism, λ_{max} is a fixed multiple of λ_{min}, and thus of R [3]. When surface diffusion dominates transport, $\lambda_{max} = \sqrt{2} \cdot \lambda_{min}$ ($\approx 8.89R$); for lattice-diffusion-controlled breakup of a pore channel, $\lambda_{max} \approx 1.459\lambda_{min}$ ($\approx 12.96R$). Thus, in principle, precise measurements of the (spherical) pore size and spacing, or measurements of the pore spacing and knowledge of R can be used to infer the transport mechanism dominating perturbation growth. These linear stability analyses also provide a means of estimating the relevant diffusivity from observed breakup kinetics.

Models for isotropic systems that consider the presence of finite-amplitude perturbations have been presented, and as the initial amplitude (α_0) increases, λ_{min} decreases [26], the kinetic maximum shifts to higher values of λ, specifically, $\lambda_{max} = [\sqrt{2} + 0.98 \cdot (\alpha_0/R)] \cdot \lambda_{min}$, and the time for pinchoff is also affected [27]. For $\alpha_0 = 0.1 \cdot R$, the rates indicated by the nonlinear analysis exceed those predicted by the linear analysis, with a 2× enhancement when $\lambda/\lambda_{min} \approx \sqrt{2}$, and a 5× enhancement when $\lambda/\lambda_{min} \approx 10$. The effect of variations in the perturbation amplitude and interactions between perturbations of differing wavelength on evolution behavior have also been considered [28] in an effort to understand the scatter in the particle spacing, L, often seen in experimental studies, and shifts to dominant wavelengths that exceed the predicted λ_{max}. Pre-existing perturbations with a normalized amplitude (α_0/R) in the range of 0.01–0.05 were found to introduce considerable scatter in L, and the average particle/pore spacing, $\overline{L}$, could approach 3× the value of λ_{max} in isotropic systems.

2.2. Modeling Rayleigh instabilities in anisotropic systems

Even more significant corrections to the behavior predicted by linear models of isotropic solids arise when the