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Reply to "Comment on 'Morphology of Silicon Nitride Grown from a Liquid Phase'"

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(1) In their comment on our paper,[1] Kitayama *et al.*[2] suggested that the weighted mean curvature method should have been used to obtain surface chemical potential. Their results are correct, but only for crystals that have a flat end. Since the grains of β-Si_3N_4 in our observation, as well as others reported in the literature, are not fully faceted and do not have flat ends, their results cannot be applied to those cases. They are certainly not useful for treating surface morphology that has undulations.[1]

(2) To allow a more general discussion not restricted to grains with flat ends, we have derived the surface potential for a rod-shaped crystal having spherical end caps and a circular cross section. The derivation, which is consistent with the weight mean curvature concept, will be published elsewhere. It finds that the condition of local equilibrium at the end surface requires

$$\sin \chi = a/b = \gamma_\perp/\gamma_\parallel \tag{1}$$

and the chemical potentials of the end surface and the side surface are, respectively,

$$\mu_\parallel = 2\gamma_\perp \Omega/a = 2\gamma_\parallel \Omega/b \tag{2}$$

$$\mu_\perp = (4L\gamma_\perp + 4b\chi\gamma_\parallel)\Omega/[4La + 2(b^2\chi - a\sqrt{b^2 - a^2})] \tag{3}$$

In the above as well as in the rest of this reply, we have used the same notation as in Ref. 1. (To view the geometric configurations, see Figs. 1 and 4 of Ref. 1 for definitions of a, b, L, and χ.) Note that when $b \gg a$, i.e., for crystals with flat ends, Eq. (3) reduces to Eq. (8) of Kitayama *et al.*

$$\mu_\perp = \gamma_\perp \Omega/a + \gamma_\parallel \Omega/L \tag{4}$$

(3) A major concern of Kitayama *et al.* is that grains with a spherical end satisfying local equilibrium has no driving force for axial growth or shrinkage. They believe the evolution of aspect ratio during the α–β phase transformation and Oswald ripening is caused by the dimensions a and L, not b. Although this aspect was not the focus of Ref. 1, we can now use Eqs. (1) and (2) to ascertain that grains with a spherical end also sense the thermodynamic requirement for reaching equilibrium, hence evolve toward an equilibrium aspect ratio. At equilibrium, $\mu_\parallel = \mu_\perp$. This

gives $b^2 = L^2 + a^2$, which, along with the local equilibrium condition, Eq. (1), specifies the equilibrium aspect ratio L/a. Further, it is easy to show that grains with spherical ends but with $b^2 > L^2 + a^2$ will grow in length, while those with $b^2 < L^2 + a^2$ will shrink in length. The above criterion of thermodynamic equilibrium entirely determines the evolution of aspect ratio if there is no concern for interface kinetics. Specifically, since all three dimensions—a, b, and L—enter the above criterion, Kitayama *et al.*'s statement that "the curvature at the end surface, b, has little effect on the morphological evolution of β-Si_3N_4 crystal, contrary to the general belief," is incorrect.

(4) In reality, silicon nitride grains tend to have atomically flat interfaces on the side. In the extreme case, this leads to interface control allowing no atom addition or removal on the side surface. Under this condition, axial growth or shrinkage is not determined by the equilibrium condition ($b^2 = L^2 + a^2$) above, but by the difference between the system driving force (chemical potential at infinity, μ_∞) and the chemical potential of the end surface, $\mu_\parallel$. Axial growth occurs if $\mu_\infty > \mu_\parallel$, as in the α–β phase transformation, while axial shrinkage occurs if $\mu_\infty < \mu_\parallel$, as some thinner (smaller a and b) grains may experience during Oswald ripening. The chemical potential of the side surface has nothing to do with axial growth or shrinkage. Neither does the aspect ratio. Specifically, it is entirely possible for $\mu_\parallel > \mu_\perp$ and yet there is still axial growth, or vice versa. This point was not appreciated by Kitayama *et al.*

(5) To formulate the concept of interface control more rigorously, we envisioned (see Ref. 1) two chemical potentials, one for atoms on the side surface, $\mu_\perp$, the other for atoms next to the side surface, μ_z. The latter atoms can be either adsorbed or still in the liquid. Although they are immediately adjacent to the surface atoms, under interface control these latter atoms can have a different potential, e.g., $\mu_z > \mu_\perp$. In Ref. 1, we assumed that there is a threshold below which there is no growth on the side surface. The extreme condition above therefore corresponds to the case when $\mu_z = \mu_\infty$ and $\mu_\infty - \mu_\perp$ is less than the threshold. On the other hand, if some free energy is dissipated in the liquid, then $\mu_z < \mu_\infty$. Nevertheless, as long as $\mu_z > \mu_\parallel$ and $\mu_z - \mu_\perp$ is less than the threshold required, there is still axial growth but no radial growth. This is the general case considered in Ref. 1. Again, axial growth has nothing to do with the chemical potential of the side surface, and it can continue even if $\mu_\parallel > \mu_\perp$.

(6) The observation of a concave shape on the end surface as reported in Ref. 1 provided direct evidence for a higher energy at the edge of the end surface than in the center. The logical conclusion is that the chemical potential on the side surface, or more generally, the chemical potential of atoms next to the side surface (μ_z), is also higher than at the end. The latter picture was used in Ref. 1 as the basis for solving the morphological problem. It is a new concept for β-Si_3N_4 but it is entirely justifiable by

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assuming interface control as we elaborated above. In this picture, the side surface emerges as most important because, under interface control, the liquid near the side surface can reach a chemical potential that is close to the system driving force at infinity (μ_∞). Therefore, the (adsorbed or liquid) atoms near the side surface become the main source of high-energy atoms that can be fed to the end surface during axial growth.

(7)   The curved surface observed in Ref. 1 is also an indication that local equilibrium (Eq. (1)) is not satisfied and that there is a continuous variation of chemical potential there. The definition of chemical potential in Ref. 1 using principal curvatures

$$\mu_r = -\gamma_\parallel \Omega(\kappa_1 + \kappa_2) \tag{5}$$

is thus required for a curved end surface and is correct. Kitayama *et al.* stated that the energy increase due to the normal displacement of the end surface is caused by the area increase of the side surface. This is true. Equating this energy increase to the total surface chemical potential on the end face, we obtain

$$\int_0^a \mu_r 2\pi r \, dr = 2\pi a \gamma_\perp \Omega \tag{6}$$

Using the definition of the chemical potential on the end face, we can integrate the left-hand side to find

$$-(dw/dr)_a = \gamma_\perp/\gamma_\parallel = \chi \tag{7}$$

which is exactly the boundary condition that we used in Ref. 1, requiring the inclined angle of the end face to be maintained at the equilibrium value. It also follows from Eq. (6) that the average chemical potential on the end surface equals the equilibrium chemical potential, $2\gamma_\perp \Omega/a$, and the average radius of principal curvatures equals the equilibrium spherical radius, $b = a/\chi$. Kitayama *et al.* stated that their weight-mean-curvature prediction ($\mu_\parallel = 2\gamma_\perp \Omega/a$) can be used to approximate the chemical potential of a curved end face. This approximation is incorrect and should be replaced by the boundary condition, Eq. (6), instead. Indeed, their approximation cannot lead to the correct solution for the shape of the end surface.

(8)   We have thus far discussed thermodynamics only. In general, once thermodynamics defines the boundary conditions, the major features of the solution and the directions of atomic fluxes are determined regardless of the details of the kinetics (surface diffusion, near-surface liquid diffusion, or liquid diffusion). In this respect, the position of Kitayama *et al.*, that surface (or interfacial) diffusion is in the opposite direction of liquid diffusion, and that the shape cannot be explained by surface (or interfacial) diffusion but can be explained by liquid diffusion, is clearly untenable.

(9)   We solved in Ref. 1 the case for surface diffusion which is mathematically expedient. Insight to the liquid diffusion problem, however, can be obtained by using the same dimensional argument embodied by Eqs. (16) to (19) of Ref. 1. We first consider liquid diffusion to occur mainly within a boundary layer of a thickness δ_ℓ. Within this approximation, the entire argument can be reestablished by replacing M_r, D_r, and δ_r in Eqs. (16) to (19) with their counterparts in the liquid—M_ℓ, D_ℓ, and δ_ℓ. This gives a shape prediction based on a dimensionless parameter S that depends on diffusivity (or mobility), radius a, and axial growth velocity only. Since liquid diffusion only directly impacts diffusivity, it does not change the main feature of the solution but merely shifts the kinetic window of shape transition.

(10)   The value of the boundary layer thickness is not known and may vary with the growth condition and geometry. For further knowledge of this parameter, a numerical solution taking into account the chemical potential of a curved surface and the boundary conditions in Ref. 1 is needed. Such a solution will be published elsewhere. For an estimate, however, we can assume the boundary layer thickness to be of the order of a. We then conclude that if $\delta_r D_r \gg a D_\ell$, surface diffusion should dominate over liquid diffusion, and vice versa.

(11)   Finally, with the above clarification and extension, we believe the analysis in Ref. 1 remains valid but needs the following corrections. Equation (2) in Ref. 1 should be replaced by Eq. (3) in this reply. Equations (4), (6), and (25) in Ref. 1 should have 2 in front of $\gamma_\perp$. There are also two typographical errors in Ref. 1. The "t" in the boundary condition following Eq. (14) should be "r", and the line before Eq. (32) should refer to Eq. (31) and not Eq. (32). Fortunately, these corrections do not enter the main results in Ref. 1, and do not affect its solution, discussion, and conclusions.

Acknowledgment

References

[1] L.-L. Wang, T.-Y. Tien, and I.-W. Chen, "Morphology of Silicon Nitride Grown from a Liquid Phase," *J. Am. Ceram. Soc.*, **81** [16] 2677–86 (1998).
[2] M. Kitayama, K. Hirao, M. Toriyama, and S. Kanzaki, "Comment on 'Morphology of Silicon Nitride Grown from a Liquid Phase,'" *J. Am. Ceram. Soc.*, **83** [3] 675–76 (2000).   □