Role of Lu and La in the intergranular films on growth of the prism surface in β -Si₃N₄: A
Molecular Dynamics Study

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Abstract

The different roles of Lu and La in the intergranular film in silicon nitride on the growth morphology are investigated via molecular dynamics simulations. While advanced microscopy shows each rare earth on the prism surface at room temperature, each additive affects the outward (perpendicular) growth of the surface differently. The simulations show the effect of elevated temperature on the adsorption of La and Lu on this surface that affects growth and provides the atomistic mechanism for the different growth morphology.

Main Text

Intergranular glassy films (IGFs) are formed at the grain boundaries from the densification additives used in many Si₃N₄ ceramics that are fabricated through liquid phase sintering. Silicon oxy-nitride sintering additives containing rare earths (RE) elements can be added to obtain a fully dense form, but also affect growth morphology and subsequent properties. The silicon nitride basal growth along the c-axis is relatively

fast while the growth of prism surface is controlled by dopant species and is relatively slow and strongly influence the grain aspect ratio and grain size distribution[1]. The dopant atoms can largely control the anisotropy of grain growth, enabling formation either of highly anisotropic grains forming the whisker-like grain morphology or of more isotropic grains[2-5]. La additive enables the highly anisotropic grains whereas Lu enables more isotropic grains, indicating a different affect of each on growth behavior. Previous simulations predicted the segregation of network modifying ions in the silicate or oxy-nitride IGFs onto the prism surface in silicon nitride[6,7] that inhibited growth of that surface along its surface normal versus growth of the basal surface, consistent with anisotropic grain growth in silicon nitride. Experiments similarly showed the presence of RE ions on the prism surface[8,9].The puzzling observation is that high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of each of the rare-earth doped IGFs show both La and Lu rare earths adsorbed onto the prism surface[9], implying similar poisoning behavior, which is clearly not the case. The question as to why the adsorbed rare earths play a significantly different role on growth is only answered by the point that Lu must be less strongly bound than La. Differences in site binding of Gd in the IGF in silicon nitride was experimentally determined[10].In order to address this point and provide a more detailed molecular mechanism, molecular dynamics(MD) simulations that provided accurate siting of La and Lu ions at the prism surface of silicon nitride [11-14]consistent with HAADF-STEM [5,8,9,15-17]were used in elevated temperature studies.Such atomistic details of the behavior of the different rare earth additives at

elevated temperature are not readily available in the experiments.

The computational system is composed of a prism oriented crystal, a high index oriented crystal, with a rare-earth doped silicon oxy-nitride intergranular film between them. The system dimension is about 9.898 nm x 5.242 nm x and initially around 7.7 nm in the x, y, and z dimensions, respectively. There are 13104 atoms in the prism crystal and 7734 atoms in the high index crystal. Around 21273 atoms for the IGF are first randomly inserted into the empty region between the differently oriented crystals. Using a melt/quench process to obtain a glassy IGF similar to previous work[13], additional long simulations at molten temperatures were used to evaluate growth at elevated temperature. Here, we focus on the simulations at 7000K for the 10 ns duration. Several IGF compositions are presented: (0.2% and 1.0% Lu or La, and 70%, 90% N/(N+O), with Si and O completing the composition in the IGF).

A multi-body interatomic potential is employed, consisting of a two-body part and a three-body part, as previously presented[11,14]. Parameters are taken from potential set A for both Lu and La interactions with anions as presented in previous work[14]. The potential well depths for these sets for RE-O are similar (La-O = -10.74 eV vs. Lu-O = -10.11 eV) and RE-N are similar (La-N = -8.68 eV vs. Lu-N = -8.78 eV).

The diametrical growth on the prism surface is found to be limited and controlled by the dopant type. Figure 1 shows snapshots of the beginning (a) and end (b) of the 1%

Lu-doped 90% N/(N+O) system and the beginning (c) and end (d) of the 1% La-doped 90% N/(N+O) system, each run at 7000K for 10 million steps. In figure 1 (a,b), the silicon nitride prism surface (crystal at bottom of images) clearly grows two full layers outward in the Lu-doped system. Some Lu clusters are formed, but this does not inhibit crystal growth. Figure 1 (b) shows that some Lu ions, which are originally on the prism surface, move away during this grain growth. In the La_2O_3 -doped system, partial growth of a slight half-layer in limited areas of the crystal surface is shown in figure 1 (c, d). The La-doped prism grain grows much less than the Lu-doped prism grain. The La ions do not form the clusters seen in the Lu system, and the surface coverage can act as pinning points on the prism surface. This largely suppresses the diametrical growth on the prism surface during the simulation. The La ions can stay stably at the adsorption sites in comparison to Lu because of their increased coordination number to N in comparison to Lu-N. The La ion size allows for higher and more uniform coordination to N (sharper first peak) than does Lu.

In Figure 2, density profiles of each species in the two crystal orientations and the IGF are shown at the start (a) and end (b) of the simulation of the 90% N/(N+O), 0.2% Lu IGF at 7000K. The prism oriented crystal is on the left of each figure and the misoriented crystal is on the right. The green dashed vertical line denotes the last full N plane in the prism surface at the start of the simulation; the red dashed vertical line denotes the last full N plane in the crystal at the end of the simulation, clearly showing growth of the prism oriented crystal. Because this is a partially oxidized nitride surface,

O is seen in some of the nitrogen sites in the prism surface. Lu ions are seen adjacent to the prism surface (green dashed line) at the start. Unlike the La ions, Lu ions at the prism surface do not inhibit grain growth, as seen in the growth shown in figure 2b. However, the figure shows that while Lu ions move away from the surface during growth (vacating the volume between the green and red lines), they remain in contact with the surface at the end.

Considering an important feature in HAADF-STEM images of Lu- and La-doped IGFs, where both of these RE ions are observed at the prism surface, the question of why one poisons growth by its presence at the surface (La) and the other does not (Lu), Figure 2 provides an answer. Lu ions remain near the surface but do not inhibit growth; they are more easily displaced as Si and N attach. Further cooling would eventually prohibit further crystal growth but the Lu would be located on the surface at lower temperature, showing up in the HAADF-STEM images. This difference between La and Lu on growth occurs in the simulations, even though the potential wells discussed above are similar for each rare earth interaction with the anions in the system.

An additional feature observed in the images shown here and additional simulations not shown is the strong tendency for formation of small clusters of Lu ions (as Lu-X, where X=O or N) that is not seen in the La case. Figure 3 shows a snapshot of the 1% Lu (a) and 1% La (b) systems with 70%N/(N+O). Since these have relatively thick IGFs (~1.8 nm), the cluster sizes in the Lu system would be larger than what has been observed in

the smaller 0.6 nm IGFs often seen in HAADF-STEM[5]. However, these Lu clusters could be correlated to the “Lu rich region” observed experimentally[5]. Speculatively, these clusters in the Lu IGF may act to deflect cracks propagating through the IGF and increase the strength of the Lu-doped systems.

Figure 4(a-d) show energies and the x-z locations of Lu ions corresponding to the initial (a,c) and final (b,d) configurations at two concentrations of N in the IGF. In all cases the Lu are bonded to anions (not shown). Figure 5(a, b) shows the sample of 90% N/(N+O) and 0.2% Lu. The Lu ions initially exist as isolated ions in each system with relatively high energies (low absolute values). Lu ions form small clusters that merge to form bigger clusters with lower energies as shown in 4b. Figure 4(c,d) shows the energies and locations of Lu ions for sample of 70% N/(N+O) and 0.2%. Smaller Lu clusters occur with more oxygen in the IGF. This fits the idea that small clusters are seen at the interface of the 0.6 nm films with HAADF-STEM[5]. The thin films potentially have more oxygen than a thicker film, because, with a given concentration of N in the IGF, the effect of depleting the IGF of one crystal layer's worth of N adsorbing onto the crystal surface would decrease the remaining N concentration more in the thinner film than in a thicker IGF.

In summary, the simulations presented here provide the mechanism for the observed presence of both Lu and La ions at the prism surface at room temperature in HAADF-STEM, potentially poisoning the surface from growth equally, yet show quite

different effects of each RE on prism growth. The simulations show that different behavior of the REs at elevated temperature significantly affects growth while maintaining the presence of each RE at the surface at lower temperature. Results show that the IGF composition plays an important role in the behavior of the Lu ions on growth. Lu ions are readily displaced by Si and anions during high temperature prism crystal growth, but remain in close contact with the growing surface. The results are not biased by significantly different potential well depths, as presented above and yet La ions adhere more strongly to the crystal surface at elevated temperatures than do Lu ions. This is due to the increased coordination number of N ions bonded to La in comparison to that to Lu (even though the La-N is slightly weaker than the Lu-N). The increased coordination, and hence binding energy, for La are due to the larger La size that more uniformly fits into the surface structure. La significantly inhibits, but does not completely stop growth while Lu allows for significantly more growth, as seen both experimentally and in these simulations. Control of the composition (Lu, N, and O) within any specific IGF between two nitride grains may be experimentally difficult, but the simulations indicate that growth would be quite different at a given temperature depending upon the local IGF composition.

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References

- [1] R.L. Satet, M.J. Hoffmann, R.M. Cannon, *Mat. Sci. Eng. A* 422 (2006) 66.
- [2] P.F. Becher, G.S. Painter, N. Shibata, R.L. Satet, M.J. Hoffmann, S.J. Pennycook, *Matl. Sci. Eng. A* 422 (2006) 85.
- [3] P.F. Becher, G.S. Painter, N. Shibata, S.B. Waters, H. Lin, *J. Am. Ceram. Soc.* 91 (2008) 2328.
- [4] R.L. Satet, M.J. Hoffmann, *J. Am. Ceram. Soc.* 88 (2005) 2485.
- [5] N. Shibata, G.S. Painter, P.F. Becher, S.J. Pennycook, *Appl. Phys. Lett.* 89 (2006) 051908.
- [6] S.H. Garofalini, W. Luo, *J. Am. Ceram. Soc.* 86 (2003) 1741.
- [7] X. Su, S.H. Garofalini, *J. Mat. Res.* 19 (2004) 3679.
- [8] N. Shibata, S.J. Pennycook, T.R. Gosnell, G.S. Painter, W.A. Shelton, P.F. Becher, *Nature* 428 (2004) 730.
- [9] G.B. Winkelman, C. Dwyer, T.S. Hudson, D. Nguyen-Mahn, M. Dobliger, R.L. Satet, M.J. Hoffmann, D.J.H. Cockayne, *Appl. Phys. Lett.* 87 (2005) 061911.
- [10] K. van Benthem, G.S. Painter, F.W. Averill, S.J. Pennycook, P.F. Becher, *Appl. Phys. Lett.* 92 (2008) 163110.
- [11] Y. Jiang, S.H. Garofalini, *J. Am. Ceram. Soc.* 93 (2010) 3886.
- [12] Y. Jiang, S.H. Garofalini, *J. Mater. Chem.* 20 (2010) 10359.
- [13] Y. Jiang, S.H. Garofalini, *Acta Mater.* 59 (2011) 5368.
- [14] Y. Jiang, S.H. Garofalini, *Acta Mater.* 66 (2014) 284.
- [15] A. Ziegler, J.C. Idrobo, M.K. Cinibulk, C. Kisielowski, N.D. Browning, R.O. Ritchie, *Science* 306 (2004) 1768.
- [16] C. Dwyer, A. Ziegler, N. Shibata, G.B. Winkelman, R.L. Satet, M.J. Hoffmann, M.K. Cinibulk, P.F. Becher, G.S. Painter, N.D. Browning, D.J.H. Cockayne, R.O. Ritchie, S.J. Pennycook, *J. Mater. Sci.* 41 (2006) 4405.
- [17] G.B. Winkelman, C. Dwyer, C. Marsh, T.S. Hudson, D. Nguyen-Mahn, M. Dobliger, D.J.H. Cockayne, *Mater. Sci. and Eng. A* 422 (2006) 77.

Figure 1. Growth behavior on the silicon nitride prism surface at 7000K for a duration of 10 ns for Lu₂O₃-doped glassy phase with 90% N/(N+O) and 1% Lu (a) start, (b) end and for La₂O₃ with 90% N/(N+O) and 1% La (c) start, (d) end. The bottom of each image is the side view of the crystal.

Figure 2. Density profiles of species of Si, N, O, and Lu as a function of z location and time $f(z,t)$ for the sample with 90% N/(N+O) and 0.2% Lu at 7000K during a 10 ns duration period at (a) start, (b) end. Two dashed lines are marked at same locations for (a) and (b) near 30Å in z to indicate the last full N plane in the crystal at the start (green) and end (red) of the run (see text).

Figure 3. Snapshots of the 1% Lu and 1% La systems with 70% N/(N+O). Black dots are the RE ions. Figures show clustering occurring in the Lu system, but no such behavior in the La system (clusters involve RE-anion bonding, no RE-RE observed). These relatively thick IGFs (~1.8nm) allow for large Lu clusters to form that might not be so large in thinner IGFs but may be present in the triple points.

Figure 4. The evolution of Lu ions start (a) and end (b) for 90% N/(N+O) and 0.2% and start (c) and end (d) for 70% N/(N+O) and 0.2% Lu. Locations of the Lu ions are projected on the x-z plane. Energies of the Lu ions are marked by colors.

Figure 1

Figure 2

Figure 3

Figure 4

At elevated temperature, Lu ions move away from the surface as it grows, but remain in near contact (a-start, b-end), whereas La ions remain at the surface and prevent growth (c-start, d-end).