[Note: This is a reprint of an abstract. Contents of this document should not be quoted or referred to without permission of the author(s).]

To be presented at Microscopy and Microanalysis 2004, the annual meeting of the Microscopy Society of America, be held in Savannah, Georgia, August 1-5, 2004.

Z-Contrast STEM Imaging of Dopant Sites in a Silicon Nitride Intergranular Film

N. Shibata[*†], G.S. Painter[**], P.F. Becher[*], and S.J. Pennycook[*]

[*]Condensed Matter Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6030

[**]Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6064

[†] JSPS Research Fellow

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-00OR22725. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

Prepared by the

CONDENSED MATTER SCIENCES DIVISION
OAK RIDGE NATIONAL LABORATORY
Managed by
UT-BATTELLE, LLC, for the
U.S. DEPARTMENT OF ENERGY
Under Contract DE-AC05-00OR22725

March 2004

Z-contrast STEM imaging of dopant sites in a silicon nitride intergranular film

N. Shibata,*†, G.S. Painter,**, P.F. Becher* and S.J. Pennycook*
* Condensed Matter Sciences Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6031
** Metals and Ceramics Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6064
† JSPS Research Fellow

Silicon nitride (Si_3N_4) ceramics are used in numerous applications because of their ability to overcome the inherent brittleness of ceramics through reinforcing microstructures with whisker-like grains [1]. However, the formation of such anisotropic grains is very sensitive to the dopant cations used in the sintering additives [2]. Understanding the underlying atomistic mechanism of these dopant effects is key to the design high-performance Si_3N_4 ceramics through microstructure optimization.

Generally, Si_3N_4 ceramics are fabricated through liquid phase sintering, where oxynitride amorphous intergranular films (IGF) with thickness on the nano-meter scale are formed between grains[3]. Dopant atoms are expected to reside in IGFs and control the anisotropic grain growth essential for the formation of a whisker-like grain morphology. However, the atomic level details about how the dopants are distributed within the IGF have been extremely difficult to assess, due to its very small thickness (i.e., < 2 nano-meters) of IGF and its amorphous nature.

Here, we show direct images of dopant atom sites (La) within the sub-nanometer IGF in La-doped Si_3N_4 using aberration corrected Z-contrast STEM[4]. Figure 1(a) is a HAADF-STEM image of the IGF region. The grain on the right is aligned with the [0001] projection of b-Si_3N_4, so that the (10**Error!**0) prismatic boundary plane is set at an 'edge on' condition. In the image, bright spots inside the grains correspond to the Si columns, and the bright vertical band at the center of the image indicates the position of the IGF, which is confirmed by the amorphous-like contrast in the BF-STEM image of the same region. The estimated IGF thickness is about 1 nm in both images. The strong bright contrast in the IGF is due to the presence of atoms with high atomic number, in this case, La (Z=57). Notice that the highest intensity in the HAADF image is observed at the IGF/grain interfaces and a minimum occurs around the center of the IGF. Figure 1(b) shows the image intensity profile across the boundary summed along Figure 1(a). It is clearly seen that the maximum intensities appear at both IGF/crystalline interfaces, resulting in a bimodal intensity distribution across the IGF. The strong zone of image intensity along the right edge of the IGF is located where the terminal Si columns in the right hand grain would have existed, suggesting that this zone represents the first cation layer of the glass attached to the b-Si_3N_4 terminating surface.

Figure 2 is a magnified HAADF-STEM image of the IGF/ prismatic crystalline interface. The b-Si_3N_4 lattice structure is superimposed on the image. Within the interfacial zone, La atoms are readily observed as bright spots (denoted by red arrows). Note that the positions of the La atoms are shifted from that expected for Si atoms for the continuation of the b-Si_3N_4 structure; these

expected positions are shown by open green circles. These La sites are in good agreement with the calculated stable positions of La at a N-terminated prismatic plane using first principles cluster calculations[4]. The present result clearly indicates that the anisotropic grain growth should be related to the strong preferential segregation of La to the prismatic planes, retarding the grain growth effectively on these specific planes.

References

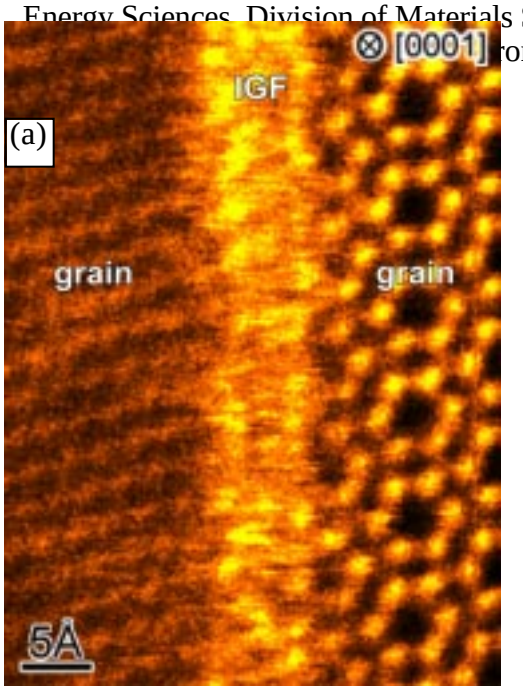
[1] I-W. Chen et al (ed), *MRS proceedings* **287** (Mater. Res. Soc. Pittsburgh, PA, 1993).

[2] Hoffmann, M.J., Gu, H & Cannon, R.M.. *Interfacial Engineering for Optimized Properties II* **586**, 65-74(Mater. Res. Soc. Warrendale, PA, 2000).

[3] Kleebe, H.-J., *J. Ceram. Soc. Jpn.* **105**, 453-475 (1997).

[4] N. Shibata et al., *Nature*, in press.

[5] We thank R. L. Satet and M. J. Hoffmann for supplying the silicon nitride ceramics used in this study. This work was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering. N.S. acknowledges the [illegible]romotion of Science (JSPS).



(b)

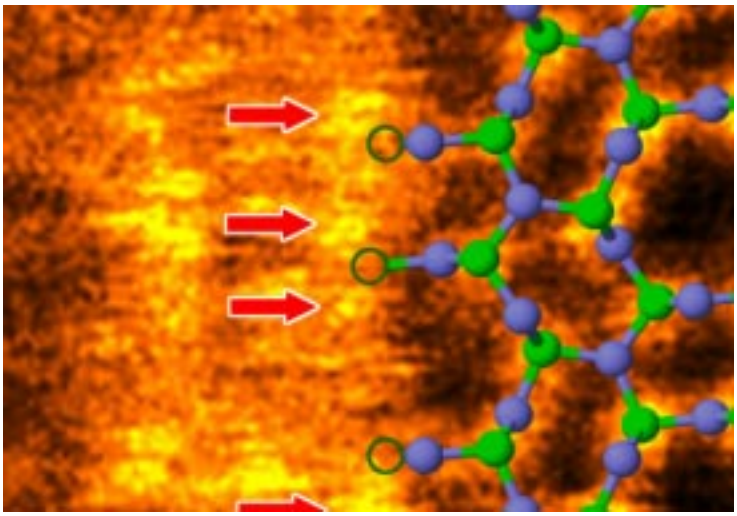


FIG.1: (a) HAADF image of IGF. (b) Image intensity profile across (a)