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STEM Characterization of Ceramic Interfaces

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Grain boundaries in ceramics play an important role on the various properties. It is well demonstrated that the addition of small amounts of dopants strongly improve the mechanical and functional properties in polycrystalline ceramics. These dopants are often segregate to grain boundaries, and change the grain boundary atomic and electronic structures. Al_2O_3 is typical structural ceramics, and the creep properties is much improved by adding lanthanoid elements such as Y and Lu . It is also well known that ZnO ceramics doped with some additives such as Pr, Bi, and Co show highly nonlinear current-voltage (*I-V*) characteristics, and thus used as varistor. So far, a number of models to explain the improvement in grain boundary properties due to heavy element impurity doping have been proposed, but the atomic-scale mechanism of how these dopants actually affect grain boundaries is still controversial. This is because the atomic location of the dopants is not clear, and how grain-boundary doping occurs on the atomic scale has not been revealed.

With recent advancements in Scanning Transmission Electron Microscopy (STEM) yielding resolutions on the scale of 0.1nm, we can now directly observe the impact of impurity doping on the grain boundary atomic structure. Z-contrast images obtained from STEM intrinsically contain chemical information due the acquisition conditions employed, and thus, the location of the dopants can often be determined from the image alone. The atomic structure of the grain boundary is often rather complicated and the use of atomic simulations, such as static lattice calculations and density functional calculations, is required to interpret the experimental results, in order to predict the properties of the structures observed from STEM. In this study, the well-defined grain boundaries in Al_2O_3 and ZnO bicrystals doped with Y and Pr were observed by using high-angle annular dark field (HAADF)-STEM. Cs-correctd-STEM was used for the present experiments (Cs-corrector attached JEM-2100F, JEOL Co. Ltd.), and the HAADF detector with an inner angle greater than 60 mrad. was used with an probe size about 0.1nm.

Fig.1 shows a Z-contrast image of the Y-doped Σ31 grain boundary in Al_2O_3 [1]. The most striking feature is the unusually bright columns that lie periodically along the boundary plane, indicating the presence of Y. The structural units observed at the Y-doped boundary closely resemble the units found in the undoped case, suggesting that Y plays little role in altering the basic grain boundary atomic structure of neighboring atomic sites. Instead it appears that Y^{3+} simply replaces Al^{3+} on the cation sublattice. According to the first principles calculations, the presence of Y at the 7-membered rings was found to increases the number of bonds, and the bond strength was increased due to the higher covalency of the Y-O bonds as shown in Fig.2 [1]. This should result in a much stronger grain boundary, which explains why the Y-doped grain boundaries can have such a large increase to creep resistance despite the fact that only a small amount of Y is present.

Fig.3(a) shows a Z-contrast image of the Pr-doped ZnO Σ7 boundaries [2]. In the image, the positions of the atomic columns are directly imaged as the bright spots. It is clearly seen that very bright spots are periodically found along the GB. Since the atomic number of Pr is larger than that of Zn, the very bright spots correspond to the presence of Pr. The Pr is only found at the specific atomic columns of the boundary plane, that is, the Pr segregates to the specific atomic sites of the boundary

plane [2]. Fig.3 (b) shows the stable atomic structure of the Pr-doped Σ7 boundary calculated by the first-principles calculations. The calculated structure is basically similar to that is deduced from the Z-contrast image. It was found that the origin of the varistor properties is due to the formation of Zn vacancies which were generated by the Pr segregation.

References

[1]] J.P.Buban, K.Matsunaga, J.Chen, N.Shibata, W.Y.Ching, T.Yamamoto and Y.Ikuhara, Science, Vol.311, (2006) 212.

[2] Y.Sato, J.P.Buban, T.Mizoguchi, N.Shibata, M.Yodogawa , T. Yamamo and Y.Ikuhara, Phys. Rev.Lett. , 97 (10), (2006) 106802.

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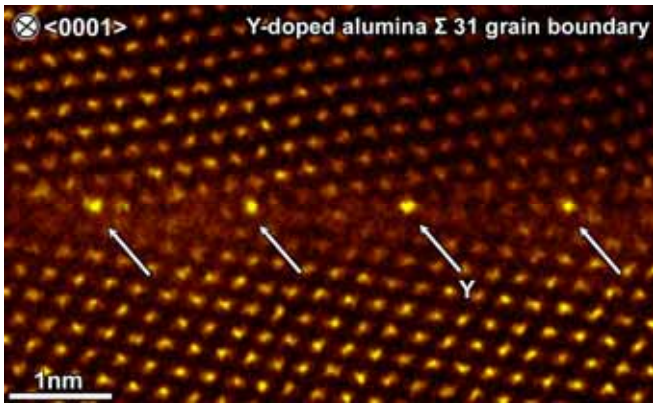

Fig.1. Z-contrast STEM image of Y-doped Σ 31 [0001] tilt grain boundary in alumina. The brightest columns indicate the presence of the heavy Y ions. These Y containing columns are found right at the center of the 7-member ring unit [1].

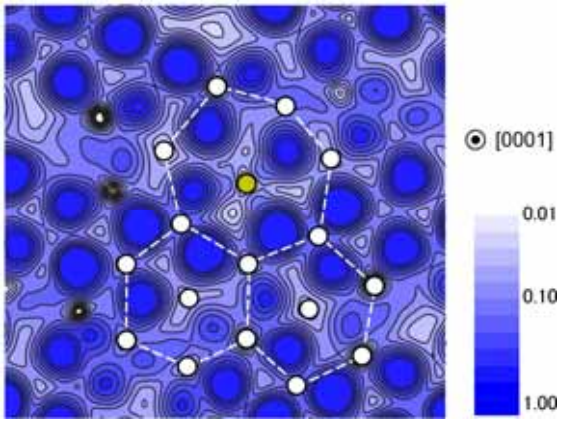

Fig.2. Electron density map around Y atoms segregated in Σ31 grain boundary, which was obtained by the first principles calculation [1].

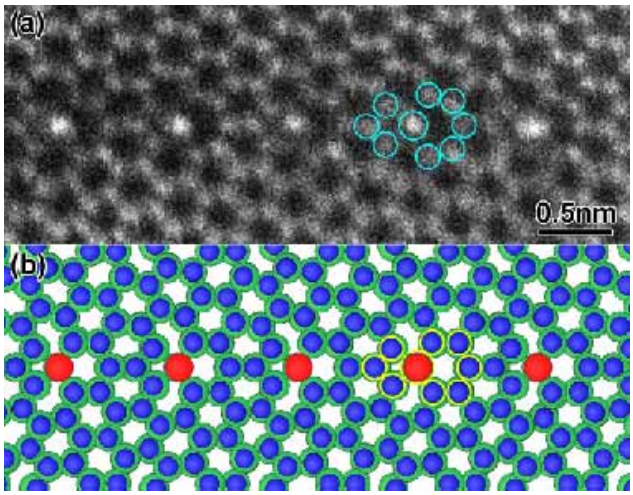

Fig.3. (a) Z-contrast image of the Pr-doped Σ7 boundary [2]. In the image, positions of the atomic columns in the boundary are superimposed by the open circles. (b) Calculated atomic structure of the Pr-doped Σ7 boundary. Blue, green, and red circles denote Zn, O, and Pr atoms, respectively. Pr atoms substitute the Zn atoms at the fivefold-coordinated sites.