MERIT Self-directed Joint Research

Dynamic STEM observation and ANN calculation of Hf diffusion in α-Al_2O_3 Σ31 GB

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Authors Introduction

Toshihiro Futazuka specializes in the theoretical calculation of the grain boundary based on the scanning transmission electron microscopy (STEM) observation. He analyzed the STEM image and carried out molecular dynamics based on artificial neural network potential.

Yuuki Nakano specializes in the development of artificial neural network potentials for oxide systems. He constructed the artificial neural network potential.

1 Introduction

The interfaces between two grains, called grain boundaries (GBs), have a significant influence on the mechanical and electrical properties of polycrystalline materials[1]. When a dopant is introduced to the polycrystal, it tends to segregate and diffuse preferentially along the GBs. This GB diffusion affects the materials properties such as grain growth and high-temperature strength[2,3]. Therefore, it is important to understand the mechanism of GB diffusion to controll the properties of polycrystalline materials.

There have been many experimental and theoretical studies on GB diffusion, but the atomistic mechanism of GB diffusion remains unclear. Traditionally, the GB has been modeled as a thin amorphous film [4]. On the basis of this assumption, the combination of the concentration measurement along GB and the mathematical model has been used to determine the GB diffusion coefficient[5–7]. However, the atomic resolution electron microscopy study has shown that GB is not an amorphous layer, but consists of a periodic array of ordered structural units[2]. This observation challenges the previous model and calls for a new theory.

To understand the mechanism of GB diffusion in atomic scale, molecular dynamics (MD) simulations have been performed. These simulations have shown that point defects, such as vacancies or interstitials, can be easily formed in the GB core, which enhances GB diffusion[8]. In addition, the ring mechanism and the collective motion of atoms play an important role in GB diffusion, although they are unfavorable mechanisms in the bulk.

However, the previous simulations face the following two challenges: (i) the lack of the direct observation of the GB transition, and (ii) the problem of the accuracy of the interatomic potentials used in the simulation. Direct observation of GB is still lacking, and it is unclear what actually happens

in the GB. In addition, the conventional interatomic potentials have difficulty in reproducing the energies of the disordered structures such as surfaces or GBs, which limits the reliability of the simulations.

In this study, we directly observe the Hf diffusion in Σ31 GB of Hf-doped α-Al_2O_3 using scanning transmission electron microscopy (STEM). We can track the dynamics of the dopants by continuously observing the same region with STEM[9]. To analyze the STEM results with MD, we develop an artificial neural network (ANN) potential for the Al-O-Hf system. ANN potentials learn the relationship between the structure and the energies calculated by density functional theory (DFT) calculations. Therefore, ANN potentials have both DFT-level accuracy and high computational speed. We reproduced the GB structure and evaluated the transition energies.

2 Method

We prepared a Hf-doped Σ31($47\bar{1}\bar{1}0$)/[0001] α-Al_2O_3 GB sample by bonding two single crystals with Hf deposited on their surfaces using physical vapor deposition. The bonding was done at 1773 K for 10 hours in air. After the bonding, we thinned the sample by mechanical polishing and Ar ion milling. We performed atomic-resolution STEM imaging with a JEM-ARM300F (JEOL Ltd.) in the University of Tokyo. The acceleration voltage was set to 300 kV, and the ADF collection semi-angles were spanned 64-200 mrad.

We constructed the ANN with a 156-78-78-1 architecture, where 156 is the number of the symmetry functions, and 78 is the number of nodes in two hidden layers. For generating the training dataset, we used the energies and forces of various structures calculated with the projector augmented wave (PAW) method implemented in VASP[10]. We prepared 39600 structures of Hf-doped α-Al_2O_3 bulk and symmetric tilt GBs around [0001] axis. The construction of ANN was done in Nagoya university.

3. Results

3.1 STEM observation of Hf-doped Σ31 α-Al_2O_3 GB.

STEM observation revealed that Hf-doped α-Al_2O_3 GB consists of the periodic array of structural units, which is similar to the pristine GB[2]. Hf atoms segregated to the GB core in Al-substitutional form. During the observation, Hf moved predominantly along the GB core, while rarely moved in the bulk region. During the observation, the framework of the GB structure was conserved, and no disconnection was observed. This result suggests that the GB diffusion of Hf occurs mainly via the vacancy exchange mechanism.

3.2 Constructing GB structure with ANN potential.

We compared the absolute energies of structures calculated with DFT and ANN for Hf diffusion in bulk α-Al_2O_3. Note that these structures are not included in the training data sets. **Figure 1** shows that

the DFT and ANN energies agree well, with a root mean square error for the energy of 4.20 meV per atom. This result indicates that our ANN potential can evaluate the activation energies of Hf transitions. We used the ANN potential to construct the observed GB structure. First, we constructed GB by relaxing the thorough rigid body translations of the two single crystals but failed to reproduce the structure. This is because the Σ31 GB is complex and has many local minima, and the system is trapped in the metastable structure. Therefore, we used the simulated annealing method[11], in which the system is cooled from high temperature. This allows the atoms to overcome the activation barriers and escape from the local minima. We performed 200 independent annealing calculations from different initial

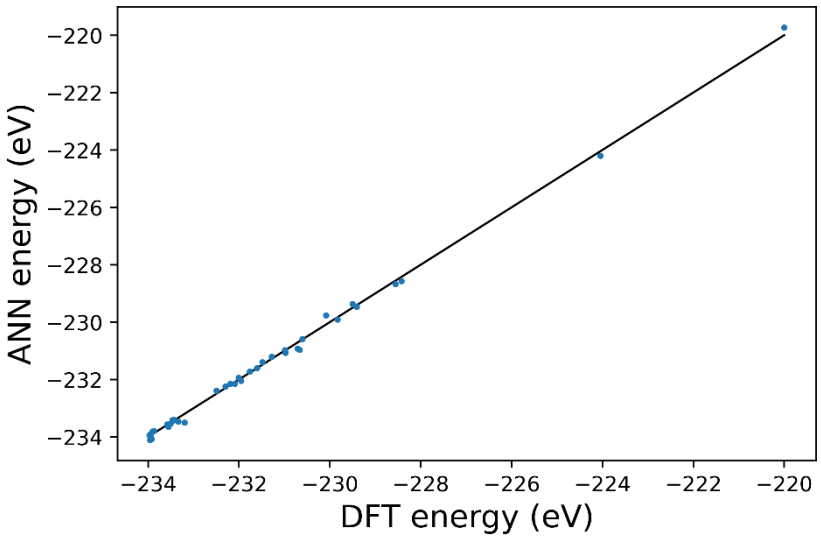

Figure 1 The relationship between DFT energy and ANN energy. The solid line is the linear fit of the data.

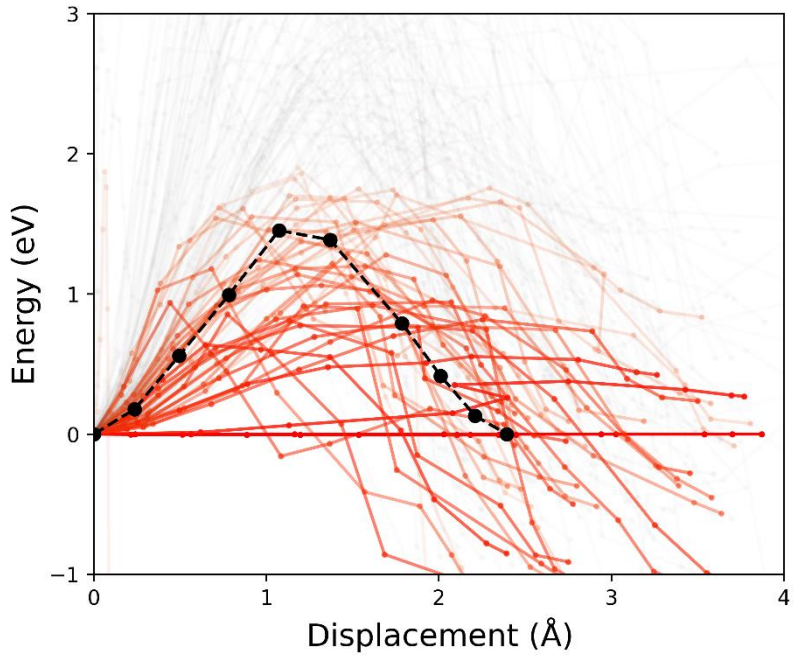

Figure 2 The energy of the vacancy exchange transitions between adjacent Al sites in Σ31 α-Al_2O_3 GB. The dashed line corresponds to the transition in the bulk.

structures and selected the most stable one. The constructed GB structure matched well with the result of the STEM observation.

3.3 NEB calculations of Hf diffusion in Σ31 α-Al_2O_3 GB.

We investigated the energetics of GB transitions based on the constructed GB structure. We assumed that Hf transitions occur via the vacancy exchange mechanism between $\mathrm{Hf}_{\mathrm{Al}}^{1+}$ and V_{Al}^{3-}. We applied the nudged elastic band (NEB) method to calculate the activation energy. NEB minimizes the total energies and of the sequence of structures (images) plus the spring energies between them. We linearly interpolated the first and last image of the vacancy exchange to generate the initial images. **Figure 2** shows the activation energy profiles obtained from NEB calculation. The dashed line represents the energy profile of vacancy exchange in bulk with the activation energy of 1.60 eV. Solid lines show the activation energies of transitions between adjacent GB sites. The activation energies vary significantly depending on the GB sites. Some GB sites have lower activation energies than that in the bulk. This reduction in the activation energy should be the origin of the enhanced diffusion along the GB.

4. Conclusion

In this study, we analyzed the GB diffusion of Hf in Σ31 $(47\overline{1}\overline{1}0)$ GB by combining the STEM observation and ANN calculation. The STEM observation revealed that Hf diffused along the GB without transforming the framework of the GB. We constructed the GB structure using simulated annealing with ANN potential and evaluated the activation energies of Hf transitions. Our calculation revealed that the Hf transition via vacancy mechanism has lower energies than that in the bulk. This reduction in the activation energy should be the origin of the enhanced GB diffusion.

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