Atomic Structure Analysis of Σ=3, 9 and 27 Boundary, and Multiple Junctions in β-SiC

Koji Tanaka, Masanori Kohyama

Special Division for Green Life Technology, National Institute of Advanced Industrial Science and Technology, AIST Kansai.

The atomic structures of Σ=3, 9 and 27 boundary, and multiple junctions in β-SiC were studied by the high-resolution electron microscopy (HREM). Especially, the existence of the variety of structures of Σ=3 incoherent twin boundaries and Σ=27 boundary was shown by HREM. The structures of Σ=3, 9 and 27 boundary were explained by structural unit models.

Introduction

There has been increasing interest in SiC as high-temperature devices or high-performance ceramics. It is very crucial to investigate the structures and properties of grain boundaries (GBs) of SiC, because grain boundaries in sintered ceramics or polycrystalline films have significant effects on bulk properties. The study of GB by the HREM is now one of the main tools for understanding materials. A rigid body translation of one grain relative to the other is an important part of the atomic relaxation of a grain boundary. The presence of a rigid body translation along the common <111> direction at Σ=3 incoherent twin boundary (ITB) was found in Si [1] and Ge [2], whereas no rigid body translation was found under different conditions in Si [1] or in diamond [3]. It was also pointed out that the translation state was sensitive to the environment of the boundary [4]. Finally, the inclination of the boundary plane can also be a possible factor in the decrease of the energy [4].

In the present study, [211]Σ=3 ITB and its junction with Σ=3 coheren twin boundaries (CTBs), [221]Σ=9 boundary and its triple junction with Σ=3 CTBs, and Σ=27 boundary and its quadruple junction with Σ=3 CTBs have been investigated by the HREM and compared with the theoretical study.

Experiment

The transmission electron microscope (TEM) specimen of chemical vapor deposition (CVD) β-SiC was prepared by the mechanical thinning and ion milling. CVD techniques can easily provide dense materials of high purity and interfaces that are well-defined even in thin films. Moreover, CVD specimens often exhibit a preferred orientation during growth and this enhances the probability of coincident site lattice (CSL) grain boundary formation. A HREM and an EELS analysis was performed on CVD β-SiC with a preferred orientation of [220] and grain size of approximately 10 μm using the field emission (FE) TEM (JEOL, JEM-3000F). Atomic models were given on the basis of the structural unit model. The relaxed atomic positions and grain boundary energies were calculated by the self-consistent tight-binding (SCTB) method.

Results

In the case of Σ=3

Figure 1 (a) ~ (d) show the atomic models of the non-polar interfaces of [211]Σ=3 ITBs in β-SiC. They include suitable reconstructions, in which arrows indicate the Σ=3 bonds. These are symmetric and asymmetric models, respectively. Type A and B are constructed for the respective models. Si atoms are reconstructed in Type A, and C atoms in Type B. The relaxed atomic positions in Fig. 1 are calculated by the SCTB method.

The wrong bonds exist at the two types of positions. These are the intergranular bonds and the Σ=3 bonds. The intergranular bonds exist on the (022) plane and cross the interface. The Σ=3 bonds that are reconstructed connect the two atoms on the neighboring (022) planes, and double the periodicity along the Σ=3 direction. The kinds and positions of the wrong bonds in Type A are inverted in Type B.

From the calculation by the SCTB method, the grain boundary energies of Fig. 1 (a) ~ (d) are 1.71, 2.37, 1.39, and 2.42 Jm⁻², respectively. Type B of the asymmetric model is the most stable and Type B of the asymmetric model has the largest energy. The energy difference between Type A of the asymmetric model and Type A of the asymmetric model is not so large, which indicates both structures can occur. The rigid-body translation in Type A of the symmetric model is a dilation of 0.001 nm and that in Type B is a dilation of 0.024 nm. The rigid-body translation in Type A of the asymmetric model is a shift of 0.072 nm along the <111> direction with a dilation of 0.016 nm. That in Type B is a shift of 0.068 nm along the <111> direction with a dilation of 0.032 nm.

Figure 2 (a) and (c) are HREM images of the [211]Σ=3 ITB in β-SiC. The length of [211]Σ=3 ITB is 6 {111} layers in Fig. 2 (a), 18 {111} layers in (c). [The lengths are indicated by numbers in Fig. 2 (a) ~ (d).] As can be easily recognized, the {111} planes on different sides of ITB reveal no shift in Fig. 2 (a), whereas no shift near the junctions with a {111}Σ=3 CTB and a shift of about one fifth of the {111} plane distance near the center of [211]Σ=3 ITB in (c). This indicates that the rigid body translation along the <111> is zero in Fig. 2 (a), and zero near the junctions and about 0.05 nm near the center in (c).

Atomic models for [211]Σ=3 ITB in Fig. 2 (a) and (c) were given on the basis of the results of the theoretical calculations. Fig. 2 (b) and (d) are structural unit models superimposed on HREM images corresponding to Fig. 2 (a) and (c), respectively. White circles represent the reconstruction along the <011> direction. It is obviously seen that the structural unit which consists of symmetric 5-7-6 membered rings align along the boundary in Fig. 2 (b), the symmetric structural units are filled in near the junction between a {111}Σ=3 CTB and a [211]Σ=3 ITB and the asymmetric structural units consisted of 5-7-6 membered rings are filled in at the middle of the [211]Σ=3 ITB in (d). All structural unit models fit with the HREM images very well. It should be noted that the positions of all white circles correspond to the Si site and it was shown that the grain boundary energy was lower when Si was reconstructed than C by the theoretical calculation.

The obtained <111> translation was approximately 0.05 nm in the experimental result and 0.072 nm in Type A in the theoretical calculation, respectively. It should be noted that the structure of [111]Σ=3 CTB plays like an anchor because it is very stable and rigid, and a [211]Σ=3 ITB always stays with a {111}Σ=3 CTB in real materials, which is essentially different from the ideal bicrystal in the simulation. At the short boundary, it is difficult to translate along the common <111> direction because the top and bottom of the [211]Σ=3 ITB are anchored by the {111}Σ=3 CTB. However, the <111> translation can occur at the relatively long boundary because...
the restriction from the \{111\}Σ=3 CTB is not so severe near the center of the \{221\}Σ=3 ITB. The reason why the experimental value is smaller than the theoretical calculation one might be that atoms can not be fully relaxed because of an anchor effect from \{111\}Σ=3 CTB.

As discussed above, the structures of \{221\}Σ=3 ITB in β-SiC were explained very well by the prediction of the SCTB calculation.

In the case of Σ=9 and triple junction

Figure 3 (a) shows an atomic model of an ideal triple junction (TJ) between one \{221\}Σ=9 and two \{111\}Σ=3 CTBs in zincblend structure along the [011] direction. It is seen from Fig. 3 (a), atoms can not have proper bonds at the \{221\}Σ=9 boundary because of the height differences in the [022] stacking. By introducing an 1/4[011] translation, the symmetric structure consisted of 5-6-7-6 membered rings can be achieved at the \{221\}Σ=9 boundary. And by introducing an 1/9[411] translation, the zigzag structure consisted of 5-7-5-7 membered rings can be achieved. It was shown that the zigzag 5-7-5-7 structure has lower energy than the symmetric 5-6-7-6 structure in Si [5]. However, introducing an 1/4[011] translation at a GB result in introducing a screw dislocation at a TJ and introducing an 1/9[411] translation result in introducing an edge dislocation. Therefore, both cases cause an increase in the total GB energy around the TJ. On the other hand, the zigzag 5-7-5-7 structure can be achieved by shifting a GB plane by one atomic column as seen in Fig. 3 (b). In this case, no extra dislocation is introduced, therefore the total GB energy around the TJ seems lower than the case of introducing a translation.

Figure 4 (a) is a HREM image of TJs between one \{221\}Σ=9 and two \{111\}Σ=3 CTBs in β-SiC and Fig. 4 (b) is a structural unit model superimposed on the HREM image corresponding to Fig. 4 (a). It is clear that the \{221\}Σ=9 boundary start from one atomic column away form the ideal TJ and the stable zigzag 5-7-5-7 structure is achieved. It should be noted that choosing a GB position has the same effect as a translation.

In the case of Σ=27 and quadruple junction

Figure 5 (a) is a HREM image of a quadruple junction (QJ) between one \{552\}Σ=27 and three \{111\}Σ=3 CTBs in β-SiC and Fig. 5 (b) is a structural unit model, superimposed on the HREM image corresponding to Fig. 5 (a). It is seen that the \{552\}Σ=27 boundary does not start from the ideal QJ and the symmetric structure consisted of 5-7-6-5-6-7 membered rings is achieved near the QJ but the zigzag structure consisted of 5-7-5-7-6 membered rings is achieved far from the QJ. The GB energy of the zigzag model is smaller than the symmetric model according to the SCTB calculation for β-SiC [6].

Figure 5 (c) and (d) are atomic models of \{552\}Σ=27 boundary. Figure 5 (c) is a symmetric model and (d) is a co-existence model of a symmetric and a zigzag structure. As indicated in Fig. 5 (c), the zigzag structure consisted of 5-7-5-7-6 membered rings like Fig. 5 (d) is achieved if the GB position shifts.
one atomic column from the symmetric structure position. To achieve the zigzag structure, an atomic relaxation is necessary. Also, the restriction from \(\{111\}\Sigma=3\) CTBs is so strong near the QJ and there is no space for an atomic relaxation. It might be the reason why the symmetric structure is achieved near the QJ and the zigzag structure is achieved far from the QJ.

**Conclusion**

The HREM and the theoretical calculation showed that the atomic structures of \(\Sigma=3, 9\) and 27 boundary, and multiple junctions in \(\beta\)-SiC were well explained by structure unit models. The translation state was sensitive to the environment of the boundary. A shift of GB position has the same effect as a rigid body translation.

**References**


![Fig. 4 HREM image of triple junctions (a) and a structural unit model superimposed on it (b). White circles represent the reconstruction along the <011> direction.](image)

![Fig. 5 (a) : HREM image of a quadruple junction between one \(\{552\}\Sigma=27\) and three \(\{111\}\Sigma=3\) boundaries in \(\beta\)-SiC. (b) : Structural unit model superimposed on (a). (c) : Symmetric model. (d) : Co-existence model of a symmetric and a zigzag structure.](image)