Atomic Structure of Faceted Σ3 CSL Grain Boundary in Silicon: HRTEM and Ab-initio Calculation

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1. Introduction

The atomic structure of Σ3 coherent and incoherent coincidence site lattice (CSL) grain boundaries has long been studied for silicon experimentally1–12) and theoretically.5–8) In particular, incoherent [112] Σ3 CSL boundary especially of covalent bonding materials such as silicon, showing unique relaxation manner with the relative rigid body translation of each grain,9–11) attracted researcher’s interest. Unique atomic structure of this boundary is expected as a source of new function which may produce quantum devices.12) If the atomic and electronic structure and their correlation are elucidated a new guideline for the design of the quantum materials would be established.

In the present study, therefore, atomic structures of the [112] Σ3 CSL boundary which is connecting corner to a [111] Σ3 CSL boundary in silicon is investigated employing high-voltage high-resolution transmission electron microscopy (HVHRTEM). The ab-initio calculation of electronic structure is performed on the lattice relaxation, the grain boundary energy and the electronic structure of the [112] Σ3 CSL boundary.

2. Experimental Procedure

A high purity polycrystalline silicon (11 nine grade) was sliced, cut and mechanically polished down to less than 10μm in thickness, and then was ion milled at 3keV acceleration. Gatan Model691 PIPS was employed. Incident angle of ion beam was fixed to be 3 degree to the specimen surface to provide a sufficiently wide area being less than 10nm in thickness. Atomic structure observation was carried out employing JEM-ARM-1300 high voltage transmission electron microscope at the Center for Advanced Research of Energy Conversion Materials (CAREM), Hokkaido University. Point to point resolution of the microscope is 0.118nm at the Scherzer defocus condition (Δf = −53nm). Projected potential atomic image is obtained at the optimum focus condition.

3. Ab-initio Calculation

In order to evaluate the stability of observed atomic structure of the [112] Σ3 CSL boundaries the ab-initio electronic structure calculation based on density-functional theory13) (DFT) using a general gradient corrected (GGA) function14) was carried out. A 96-atoms super-cell was used on the calculation. Periodicity normal to the CSL boundary was imposed by stacking symmetric boundary planes alternately in addition to the two-dimensional periodicity of the boundary. The relaxed atomic structure, total energy and electronic density of state (DOS) of the system were then calculated by norm-conserving pseudo-potential method using PHASE code.15) The plane-wave cutoff energy was set to 20Ry. The Brillouin zone integration was carried out on equivalent Monkhorst–Pack k-point mesh16) with special k-points.

4. Results and Discussions

4.1 Geometry

Figure 1 shows (a) wide view of a silicon {112} Σ3 CSL grain boundary observed in [110] direction and the magnified segmental image (b) near the connecting corner to the [111] Σ3 CSL boundary and (c) long central region. The thickness of the sample was about 8nm and the amount of defocus was almost equal to Scherzer defocus.

In Fig. 1(b) one can trace (111) plane by a straight line across the [112] Σ3 boundary as is shown by L1, R1. In Fig. 1(c), however, the (111) plane is stepped at the boundary as is seen from L3 and R3. Even in the Fig. 1(b) the (111) plane is stepped at the boundary in the region being not very close to the adjacent [111] Σ3 CSL boundary as is shown by L2 and R2. The step height was measured to be 0.15 a0[111] in average. Ratio that the step of (111) plane occupied at the observed [112] S3 CSL boundary is much greater than that of the non-stepped boundary. In other word, rigid body translation of one crystal occurred in the most part of the boundary in (111) direction (0.15 a0[111] in amount),
similarly to a previous report by Sawada et al. The amount of the translation rapidly decreased approaching to the connecting corner to the \{111\} CSL boundary. Geometrical restraint of surrounding grains prevented from the displacement in the region close to the corner.

### 4.2 Atomic structure

Further magnified atomic structure image of the central region of Figure 1(a) is shown in Fig. 2(a) and a geometrical atomic structure model is superimposed on the picture in Fig. 2(b), showing nice matching. The \{110\} Si-Si atomic dumbbell appears in dark rod-shaped contrast in Fig. 2(a). A single atomic column appears in dark round-shaped spots, being half of the rod like one in size. One periodic unit of the boundary consisted of one 7-membered ring, one 5-membered ring and one distorted 6-membered ring (Fig. 2(b)) where the atomic positions of Si-Si dumbbell are shown in a combination of white and light-gray circles, and the single atoms are shown in dark-gray circles. A geometrical structure model based on the atomic structure observation tells that an atom in the single atomic columnar site should lie on the same lattice plane with the atoms marked by neighboring light-gray circle, so that each single atom should have 3-fold coordination number.

Starting from this model, i.e., experimentally obtained geometrical atomic model, the *ab-initio* calculation was performed to obtain a relaxed structure. Figures of the relaxed structure of \{110\} and \{111\} projection are shown in Fig. 2(c) and (d), respectively. The atoms of the single atomic columns are indexed by “R” in the figures. In the \{110\} projection (Fig. 2(c)), no change was seen between starting experimental structure and the resulted relaxed structure. The step of (111) plane at the boundary was also remained. Occurred change due to relaxation is seen from the \{111\} projection in Fig. 2(c). Atoms in the single atomic column alternatively displaced in the same direction, which were \{111\} and \{111\} so that a new covalent bond was formed between the both neighboring 3-fold-coordinated atoms. A noticeable difference between initial and the relaxed structures is shown in Fig. 3. The distance of 0.386 nm between each 3-fold-coordinated atom which corresponded to \{110\} lattice plane spacing was changed to 0.245 nm due to the displacement along the \{110\} and \{110\} directions. This is a value of 104% of the equilibrium interatomic distance in bulk silicon (0.235 nm) so that neighboring 3-fold-coordinated atoms bound together. The relaxed atomic structure was...
similar to that of \textit{pm}(1x2) model proposed by Papon \textit{et al.}\textsuperscript{17)}

Calculated grain boundary energy was 0.56 J/m\(^2\), which suggests that this atomic structure is one of the most stable one. Thus, the observed asymmetric structure of the \{112\} \(\Sigma 3\) CSL boundary would minimize bond strain without introducing any coordination number defect. Any defect state due to particular atomic structure was not recognized in the band gap of crystalline bulk silicon.

A magnified atomic structure image observed in the region connecting to the \{111\} \(\Sigma 3\) CSL boundary apparently differed from that of central region (Fig. 4 (a), (b)). Atomic structure was quite symmetrical. A periodic structure unit of the boundary in this region consisted of one 7-membered ring, one 5-membered ring and one 6-membered ring.

Geometrical consideration suggests that the atom indexed by “5” in the figure has to be 5-fold-coordination. Although basic coordination number in silicon which is cohesive of sp\(^3\) covalent bonding is four it was pointed out that the existence of 5-fold-coordinated atom, so-called “floating bond”, is not unreasonable in the amorphous silicon.\textsuperscript{18,19)} Since Stich’s 5-fold-bonding consists of four ordinary bonds and one elongated bond presently observed structure\textsuperscript{19)} is not exactly same as the case. However, the 5-fold-coordination can occur in the non-periodic disordered structure such as grain boundary. Presently observed structure did not coincide with Kohyama’s model\textsuperscript{5)} of the \{112\} \(\Sigma 3\) CSL boundary which has no coordination defects, too.

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**Fig. 2** (a) A structure image of the \{112\} \(\Sigma 3\) CSL boundary and (b) a geometrical atomic structure model superimposed on (a). (c) Relaxed structure of [1\(\bar{1}\)0] and (d) [1\(\bar{1}\)1] projection obtained by \textit{ab-initio} calculation. Index “R” denotes the atoms of the single atomic columns.

**Fig. 3** [1\(\bar{1}\)1] projection images of (a) a geometrical atomic structure model and (b) a relaxed structure obtained by \textit{ab-initio} calculation.
4.3 DOS calculation

Started by the geometrical model deduced from the HRTEM observation (Fig. 4(a)), having the coordination defect, further structure relaxation of the boundary took place in a computer employing ab-initio method. The relaxed structure is shown in Fig. 4(c) and (d). In the projected atomic model in the [110] direction, the relaxed structure well matched with the observed structural image showing that the 5-fold-coordinated atom can sit without any bond reconstruction after the relaxation as shown in the [111] projection image. The calculated grain boundary energy was
0.76 J/m², which was slightly higher by 0.2 J/m² compared with the value of the stable boundary structure as is shown in Fig. 2. This implies that the atomic structure with the 5-fold-coordinated atoms is one of the meta-stable structures of {112} Σ3 CSL boundary. Such a meta-stable structure must be aided by the geometrical restriction of the adjacent {111} Σ3 CSL boundary. DOS of this boundary was calculated and was compared with that of silicon crystal (Fig. 5). A new band gap appeared near the Fermi level of silicon crystal (dotted line). New states (level) were produced in the both upper and lower side of Fermi level in the band gap. Abovementioned change is attributable to the 5-fold-coordinated atoms because it occurred only in the symmetric boundary segment. The new state, therefore, is called as defect states. The partial charge densities of the unoccupied (upper side on the Fermi level) and occupied (lower side on the Fermi level) states were visualized in Fig. 5(b) and (c) respectively. The both show that an origin of the defect states in the band gap was attributable to the localized electrons around the 5-fold-coordinated atoms.

5. Summary

The atomic structures of a {112} Σ3 CSL boundary was investigated by HRHVTEM observation and ab-initio calculation. Most stable atomic structure of the boundary was asymmetry, corresponded to rigid translation of a crystal along the interface in {111} direction. A periodic unit consisted of one 7-membered ring, one 5-membered ring and one distorted 6-membered ring, each of which was asymmetry in shape. While, the segment near the connection to {111} Σ3 CSL boundary consisted of one 5-fold and one 7-fold and one 6-fold coordinated rings, being symmetry. Ab-initio calculation showed that the atomic structure of the boundary containing the 5-fold coordinated atoms was one of the meta-stable structures of {112} Σ3 CSL boundary. Defect states which were created in the band gap at the upper and lower side of the Fermi level were shown to be attributed to the 5-fold-coordinated atom. Any defect state was not seen in the DOS of the stable {112} Σ3 CSL boundary. It was suggested that the defect states was originated in the localized electrons around the 5-fold-coordinated atoms.

REFERENCES