**Ab initio** Studies on the Effects of Si and S Impurities on Al Grain Boundary

Guang-Hong Lu1, *, Masanori Kohyama2 and Ryoichi Yamamoto1

1 Center for Collaborative Research, University of Tokyo, Tokyo 153-8904, Japan  
2 Special Division of Green Life Technology, AIST Kansai, Ikeda 563-8577, Japan

The electronic structure of Al grain boundary with segregated Si and S impurity atoms, respectively, is calculated by first principles pseudopotential method. It is found that the segregated Si atom bonds the neighboring Al atoms, forming the metallic-covalent character mixing bonds. These bonds will promote the rearrangement of atoms, such as sliding under stress. Therefore the embrittlement promoted by Si segregation should be classified into ‘bond mobility model’. However, the segregated S atom bonds only one of the neighboring Al atoms, forming a metallic-covalent character mixing bond. Other Al-S bonds in the boundary may become weaker than the former Al-Al bonds. Therefore it can’t be decided that the mechanism of the embrittlement promoted by S segregation is classified into ‘bond mobility model’ or ‘decohesion model’.

(Received May 7, 2001; Accepted June 8, 2001)

**Keywords**: first principles, pseudopotential, impurity segregation, aluminum grain boundary

---

1. Introduction

It has been found recently by the experiment that S promotes the embrittlement on Al alloys. It has been reported that the ductility of Al-Cu alloy decreases significantly if a small amount of S was added in Al-Cu alloy aged at 130 and 190°C. S was detected by Auger Electron Spectroscopy (AES) in intergranular fractal surface, which indicates that the embrittlement is caused by the boundary segregation of S. As for Si, Hinode, et al. reported that the precipitated Si promotes the nucleation and growth of the voids of the Al conductor films for LSI use and thus degrades the reliability of performance of LSI. Therefore in this paper we carry out the calculation of the effects of the Si and S impurity segregation on the Si grain boundary. Results show that it is of great interest to compare the effects of Si and S impurity on the Al boundary.

It seems that, theoretically, there are two kinds of mechanism of impurity-promoted embrittlement of metal grain boundaries. One is ‘bond mobility model’ proposed by Haydock. In this model, segregated non-metallic impurities at the metal boundary change the character of atomic bonds. For example, the impurity-metal bonds contain covalent character due to the segregation of the impurity and their mobility is reduced. Under stress, such bonds cannot slide smoothly and thus stress concentration is generated. Goodwin et al. carried out the supercell calculation on the embrittlement by Ge and As impurities in the host Al based on the density functional theory (DFT), supporting Haydock’s model. Ogata et al. performed first-principles calculations of the Al$_5$S grain boundary with Si impurities, and found that some kind of local strong bond forms between Al and Si atoms. This seems to prevent relative sliding motion along the boundary, which is consistent with Haydock’s model.

The other mechanism of impurity-promoted embrittlement of metal boundaries is called ‘decohesion model’. In this model, the intergranular cohesion is weakened due to the weak metal-impurity bonds or metal-metal bonds by the presence of impurities and thus induces embrittlement. For example, Losch presented a model that the metal-metal bonds neighboring to the impurity-metal bonds are weakened by the embrittling element in group IV-VI. Briant and Messmer calculated, on respectively, a Ni cluster with S impurity, and an Fe cluster with P impurity by cluster method. The calculations support Losch’s model. The authors carried out the calculation of the effects of Na and Ca’s segregation on Al$_5$S grain boundary and found that the weak Al-impurity bonds should reduce the intergranular cohesion and thus the embrittled mechanism should be one kind of ‘decohesion model’.

We don’t consider the lattice vibration due to the limited computational ability, and calculate the atomic and electronic structure of Al boundary at absolute 0 K. Hence the calculation results probably can’t compare directly with the experimental ones. However, our results still will be very helpful to understand the effects of Si and S impurities on the Al boundary.

2. Computational Method

The unit cell including 84 atoms is shown in Fig. 1. The length of side a, b, c are 2.8469 nm, 0.8739 nm and 0.5586 nm, respectively. Al$_5$S$_9$(221)/[110] ilt grain boundary is formed by rotating one grain by 38.94° along the [110] axis, and (221) is set as the boundary plane. The coincidence site lattice (CSL) unit cell on the boundary plane is defined by $3\sqrt{2}/a_0[114]$ and $\sqrt{2}/a_0[110]$. The size in the [110] direction is set twice that of the CSL, i.e., $\sqrt{2}a_0$, in order to isolate four impurity atoms and keep the symmetry. In the [221] direction two symmetric boundaries are introduced to make three dimensional periodicity. The distance between the grains is determined by that the atom density in boundary is the same as that of the unit cell constructed by Mills and Daw.

First principles plane-wave pseudopotential method has been used based on density functional theory (DFT) with local density approximation (LDA). The electronic ground
state is obtained using the conjugate-gradient technique proposed by Bylander, Kleinman and Lee\textsuperscript{17} with the Kerker mixing scheme.\textsuperscript{18} This method has been shown to be very efficient for determining the minimum of the Kohn-Sham energy functional for large systems containing metallic bonding.\textsuperscript{19} The plane wave energy cutoff is 13Ry, and 32 k points in the Brillouin zone is used. The charge density is determined on a real space grid of 128 × 64 × 32 points. All the atoms are relaxed according to the Hellmann-Feynman forces until all the forces are less than 0.5 eV/nm (1 eV = 1.602 × 10\textsuperscript{-19} J). TM-type\textsuperscript{20} pseudopotentials are constructed for Al\textsuperscript{21} and S.\textsuperscript{22} HSC type pseudopotential\textsuperscript{23,24} is constructed for Si.\textsuperscript{21} The separable form by Kleinman and Bylander\textsuperscript{25} with the p as the local component is used.

3. Results and Discussions

The relaxed atomic configurations are shown in Fig. 2. Only the left half parts of the first and second layer are shown due to the symmetry. E is the position of the Si or S atom in the substitutional case. The interatomic distances between the five atoms (G, F, E, H and J) are calculated and listed in Table 1. In the case of Si (Fig. 2(a)), Al atoms around the Si atom get nearer to the Si atom compared to the relaxed configuration of pure Al boundary. As in Table 1, EF\textsubscript{Al} = 0.2611 nm < EF\textsubscript{Al} = 0.2622 nm, about 0.4% decrease; EH\textsubscript{Si} = 0.2737 nm > EH\textsubscript{Al} = 0.2764 nm, about 1.0% decrease. The results of the S case (Fig. 2(b)) is different from that of the Si case. Al atom F neighbor to the S atom gets nearer to the S atom (E) compared with the relaxed configuration of pure Al boundary. On the contrary, the neighboring Al atoms except atom F all gets farther away from the S atom. For example, as shown in Table 1: EF\textsubscript{S} = 0.2558 nm < EF\textsubscript{Al} = 0.2622 nm, about 2.4% decrease; EH\textsubscript{S} = 0.2806 nm > EH\textsubscript{Al} = 0.2764 nm, about 1.5% increase.

Figure 3 shows the contours of the valence charge density of the second layer in the unit cell. There exist the impurity atoms in this layer. Only the left half part of this layer is shown due to the symmetry of the unit cell. Comparing Fig. 3(b) with (a), it can be noted that the charge density is much higher around the Si atom, especially between atoms E and F. The charge density is mainly localized between the Si atom and the neighboring Al atom. Comparing Fig. 3(c) with (a), it can be noted that the charge density is much higher between S atom and Al atom F, but becomes lower between S atom and Al atom H. This is different from that of Si case. In both cases the charge distribution between E and F atom is directional and deviates to impurity atom E.

The Si atom has 4 valence electrons and the S atom has 6 valence electrons, more than that of Al atom (3 valence electrons). This causes significant charge increase around the Si or S atom. The distance decrease of EF induces a further charge density increase between E and F atom.

The calculation range of local density of states (LDOS) is shown in Fig. 4(a). The figure shows cross section of [110] direction of the unit cell, which is perpendicular to boundary plane (221). The calculation range is the sum of two symmet-

![Diagram](image-url)
Fig. 3 Contours of the valence charge density of the left half part of the second layer in the unit cell, in which Al atoms are replaced by impurity atoms. The interval of the contours is 0.004/a.u. G, F, E, H and J correspond to the atoms marked in Fig. 1. [110] and [001] indicated in the figures are lattice directions in the grains that the grain boundary is made up of. (a) pure Al boundary (b) Si segregation (c) S segregation.

Fig. 4 (a) The calculation range of local density of states (LDOS) (b) LDOS of the range above. The solid line is the LDOS result of pure Al boundary; the dotted line and the dashed line is that of S and Si segregation case, respectively. $E_F$ (Fermi energy) is set as zero for all the three cases. $1\text{Ry} = 13.6056 \text{eV} = 2.1796 \times 10^{-18} \text{J}$.

der stress. Therefore the mechanism of embrittlement by Si segregation can be classified as the ‘bond mobility model’.

For the case of S segregation, there is a smaller peak in the middle energy region (about $-0.4\text{Ry}$) comparing with that of pure Al boundary. The same as the Si’s case, this means there exists the stronger bond than Al metallic binding in the boundary. Because S is also a covalent binding element, this bond (EF bond) should be a metallic-covalent character mixing bond. The center of gravity of the bond deviates towards S atom. However, different from the Si’s case, S atom forms stronger bond with only one neighboring Al atom (i.e. atom F). Because the charge density between E and H atom decreases, it is possible that EH bond becomes weaker than the former Al–Al bond. Therefore it can’t be decided that the mechanism of embrittlement by sulfur segregation is classified into the ‘bond mobility model’ or ‘decohesion model’.

There is another obvious increase of LDOS in the low energy region (about $-1.0\text{Ry}$) where LDOS of pure Al boundary is zero for the case of S segregation. This increase should correspond to 3s band of S, which means 3s electrons of S atom don’t participate in Al–S bond forming. The smaller peak at the energy of $-0.4\text{Ry}$ should correspond to 3p band of S atom, which means that 3p electrons of S atom participate in the stronger Al–S bond forming. For the case of Si segregation, as discussed above, there is an increase of LDOS in the low energy region (about $-0.75\text{Ry}$). This should correspond to 3s band of silicon atom, which means 3 s electrons of Si atom participate in Al–Si bond forming.

4. Conclusions

Si and S segregation both causes an increase of charge density between Si or S atom and the neighboring Al atom. There forms a bond stronger than metallic bond between impurity atom and neighboring Al atom. This kind of bond should be a mixture of covalent and metallic character. The bond should have localized, rigid and directional characters, and thus prevent the rearrangement of atoms, such as sliding under stress. However, different from the case of Si, some Al–S bonds may
become weaker than the former Al–Al bonds because of the charge density decrease. Therefore the mechanism of embrittlement promoted by Si segregation can be classified as the ‘bond mobility model’. However, it cannot be decided that the mechanism of the embrittlement promoted by S segregation is classified into ‘bond mobility model’ or ‘ decohesion model’. Further study of ‘first principles tensile test’ on the Al–S system is being carried out on the same unit cell in order to investigate if the embrittlement mechanism is classified into ‘decohesion model’.

Acknowledgements

The research is supported by the Science and Technology Agency of Japan as the joint research with National Research Institute for Metals (NRIM), and also partly supported by the Science and Technology Promotion of Japan.

REFERENCES