Transactions of the Materials Research Society of Japan. Vol. 20

Density Functional Calculation of Effect of Silicon Impurity to Aluminum $\Sigma = 5[001]$ Tilt and Twist Grain Boundary

S.Ogata and H.Kitagawa

Department of Mechanical Engineering of Osaka University, Osaka 565, Japan

The atomic structures of aluminum $\Sigma = 5[001]$ tilt and twist grain boundaries with silicon impurity are determined by using the molecular dynamics annealing simulations based on the LDA-DFT (Local Density Functional Approximation to Density Functional Theory) and effects of Si impurity to these grain boundaries are discussed. We find that if the Si-atoms exist in neighboring site of the tilt grain boundary, a prism structure including the Si-atom at the center is formed and the grain boundary stiffness changes remarkably. On the other hand, Si-atom gives a little effect concerning on the twist grain boundary.

1. INTRODUCTION

As feature size of large scale integrated(LSI) circuit being smaller, existence of defects in metal line becomes major reason of decreasing the reliability of performance of LSI. A grain boundary is a typical defect of most of the circuits which is usually made of polycrystalline metal. Since an atomic self-diffusion near the grain boundary in the Al line leads to formation of a void and finally to break down, research in detail on the grain boundary structure is vary interest and important.

Usually Al interconnect used in LSI circuits contain 1%wt Si impurity to control the reaction with a substrate or a passivasion film [1]. Hinode *et al* [2] and Lin*et al*[3] reported that the precipitated Si is a cause of generation and growth of a void and it degrades the reliability of performance of LSI. Hence, the interaction between the grain boundary and the precipitated Si may also be important problem. The grain boundary properties are definitely characterized by atomic structure near the grain boundary.

In this paper, we calculate atomic structures of the Al $\Sigma = 5[001]$ tilt and twist grain boundary, including substitutional Si-atom, by simulation based on density functional theory(DFT), and discuss the effect of the Si-atom on the grain boundary.

The LDA-DFT may overcome difficulty to estimate the atomic interactions between different kind of atoms, (e.g. between Al and Si in our calculation), which always come out in a classical atomic simulation. Since self-consistent electronic states is determined by this theory, it can be applied in principle to any materials and systems, and it is known that it gives a result with quantitatively high accuracy.

2. METHOD

We used a plane wave representation for solution of Kohn-Sham equations[4] (one-electron equation) derived on the basis of the density functional theory [5] which should be solved self-consistently. The local density approximation is adopted to describe the exchange-correlation energy as a functional of the electron density which was proposed by Perdew and Zunger[6]. The pseudopotential approximation is also used for representation of the electron-ion interactions in order to reduce a necessary number of plane waves. The *ab-initio* norm conserving pseudopotential which is proposed by Bachelet *et al.*[7] is applied to the potential form, and the plane wave

cutoff energy is set to be 12Ry. The Brillouin zone(BZ) k integration is performed by the special points method of Monkhorst and Pack's [8]. According to these treatments, the lattice constant of Si and Al can be estimated with in the only 0.2~0.9% error to experimental values extrapolated to zero temperature, which has been reported by Wyckoff[9] and is confirmed in preliminary calculation.

The Car-Parrinello algorithm[10] is employed to do dynamic simulations, and an artificial energy dissipation term is brought into the fictitious equation of motion for electron system to make the progress of the calculation more stable. The motion of the atomic nucleuses is calculated by integration of the classical equation of motion subject to Hellmann-Feynman force.

3. RESULT AND DISCUSSION

3.1. MODELS AND CALCULATION CONDITIONS

A basic $\Sigma = 5[001]$ tilt and twist pure grain boundary models used in analysis are shown in Fig.1. These models include 38 and 40 atoms, respectively. For twist grain boundaries three type models (i.e. CSL, type1 and type2) are investigated. The type1 and type2 are sliding models which are constructed from CSL structure by relative slide by 1/10 CSL length between the upper and the lower block on the grain boundary plane along x and x,y direction, respectively. These sliding models are also candidate of the lowest energy structure[11]. The periodic boundary conditions are imposed along x, y and z directions. At first, relaxed atomic configurations and cell shapes are calculated for each model by pressure constant annealing calculation based on effective medium theory[12](EMT-MD). Next, *ab-initio* calculation to determine the pure Al grain boundary structures by using a simulated annealing technique is performed, taking the EMT-MD result as an initial atomic configuration. Through out this paper it is assumed that when the atomic force for each atom becomes $F_i \leq 1.0 \times 10^{-3}$ a.u., the atomic structure is regarded to be enoughly relaxed and the calculation process is stopped.

It is found that the type1 has the lowest grain boundary excess energy among the analyzed twist grain boundaries. Hence, the following calculation with respect to the twist grain boundary is done only for type1.

3.2. ATOMIC STRUCTURE OF SI PRECIPITATED GRAIN BOUNDARY

To estimate effects of Si on the grain boundary, we assume that Si-atom exists on each grain boundary surface. The annealing calculation is done to obtain the (quasi-)stable atomic structure. The results are presented in Fig. 2. While no significantly structural changes are recognized in type1 twist case, it is found in the tilt case that Al trigonal prism structure with Si which is illustrated in Fig.3, is formed on the grain boundary and Al-atoms outside the structure move away from it. Fig. 4 shows the valence electron density distributions for the annealed atomic structures of the tilt case. The electron localizes around Si-atom and forms a firm prism structure as the result that Si binds strongly to Al-atoms. However, there exists a region where the valence electron density is very low outside the prism, being much lower than that of the grain boundary without Si-atom. This fact implies that the precipitated Si-atom perhaps makes a weak bonding region which may act as an initiator of void nucleation and promoter of its growth near the grain boundary. And the existence of a strong prism structure prevents a dislocation glide along the grain boundary. Therefore, it may cause the grain boundary to be brittle. Ishida *et al*[13] analyzed the Fe $\Sigma = 5$ grain boundary with segregated P atoms by molecular dynamics simulation. They had predicted that P centered Fe_3P trigonal structure is formed and it disturbs a dislocation glide along the grain boundary. In the twist case, however, the valence electron distribution has also a trend to localize around the Si-atom as

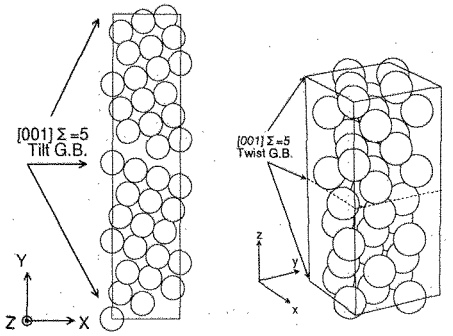

Figure 1: Model cells for $\Sigma = 5$ [001] tilt(left) and twist(right) grain boundary

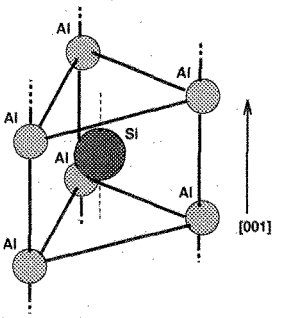

Figure 3: Unit of triangle prism structure with Si in $\Sigma = 5$[001] tilt grain boundary

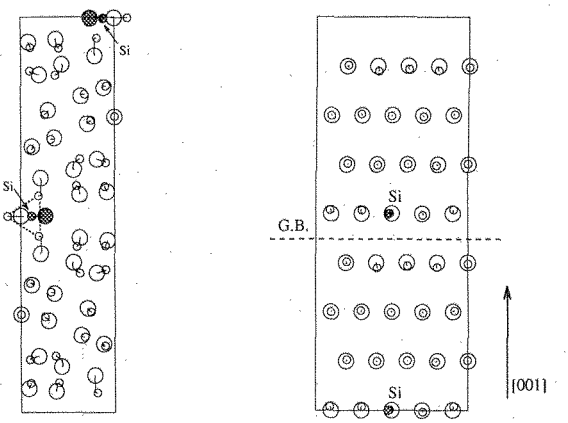

Figure 2: Atomic structure of Si precipitated $\Sigma = 5$[001] tilt(left) and twist(right) grain boundary. Large and small circle represent initial and relaxed atomic position, respectively. Si-atoms are represented by gray circle.

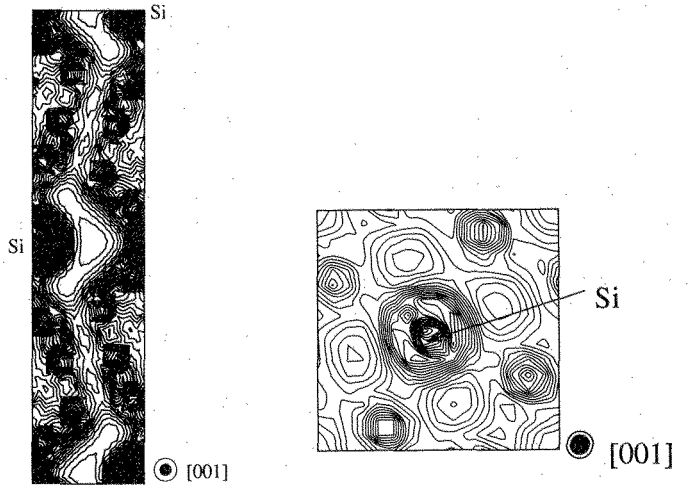

Figure 4: Valence electron density of $\Sigma = 5$[001] tilt(left) and twist(right) grain boundary with precipitated Si-atoms. The interval of contour is 2.5×10^{-3} in atomic unit.

Table 1: Force constants of tilt grain boundaries par unit area

	Non Si(Tilt) $\times 10^{20}$ N/m^3	With Si(Tilt) $\times 10^{20}$ N/m^3	Non Si (Twist) $\times 10^{20}$ N/m^3	With Si (Twist) $\times 10^{20}$ N/m^3
Normal	7.91	7.20	2.31	2.41
Shear	1.49	4.92	—	—

shown in Fig.4, it is not remarkable.

3.3. STIFFNESS ESTIMATION OF SI PRECIPITATED GRAIN BOUNDARY

To estimate changes of the grain boundary stiffness due to Si precipitation, the upper half layers in the model cell are shifted by 0.1% of the cell length in the normal and shear directions relative to the grain boundary plane and force constant is calculated. For the twist case the calculation is done only in normal direction. Calculated force constants are listed in Table1. For the tilt case, the force constant in the normal direction slightly decreases due to existence of Si but the shearing stiffness rises because the trigonal prism structure prevents relative gliding motion along the grain boundary. On the other hand, in the twist case, Si-atom increases slightly the normal stiffness.

4. CONCLUSION

The main results obtained are summarized as follows.

1. For the tilt grain boundary, the strong Si centered prism structure is formed at the grain boundary.

2. The precipitated Si-atom makes weak bonding region outer the prism structure. It decreases slightly the normal stiffness of the grain boundary.

3. The shear stiffness increases because the prism structure locks the gliding of grain boundary. This fact may read to a grain boundary embrittlement.

4. For the twist grain boundary, it seems that the Si-atom plays no important role.

References

[1] Hidekazu O., *OYO BUTURI*, **59**-11 (1990), 1461.

[2] Hinode K., Owada N., Nishida T. and Mukai K., *J. Vac Sci. Technol. B*, **5**-2 (1987), 518.

[3] Lin M.R. and Yue J.T.,*Proc. Int. Reliability Physics Symp., Anaheim*, (1986), 164.

[4] Kohn W. and Sham L.J., *Phys. Rev.*, **140** (1965), A1133.

[5] Hohenberg P. and Kohn W., *Phys. Rev.*, **136** (1964), 3864.

[6] Perdew,J. and Zunger A., *Phys. Rev., B* ,**23** (1981), 5048.

[7] Bachelet G.B., Hamann D.R. and Schlüter M., *Phys. Rev., B*, **26**-8 (1982), 4199.

[8] Monkhorst H.J. and Pack J.D., *Phys. Rev., B.*, **13**, (1976), 5188.

[9] Wyckoff R.W.G., *Crystal Structure*, (Interscience, New York, 1963).

[10] Car R. and Parrinello M., *Phys. Rev. Lett.*, **55**-22 (1985), 2471.

[11] Bristowe P.D. and Crocker A.G., *Philos. Mag., A*, **38**-5 (1978), 487.

[12] Jacobsen K.W., Nørskov J.K. and Puska M.J., *Phys. Rev., B*, **35**-14 (1987), 7423.

[13] Ishida,Y., Mori,M. and Hashimoto,M., *Surf. Sci.*, **144** (1984), 253.