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First-principles study of the effects of segregated Ga on an Al grain boundary

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Abstract

The effects of different amounts of segregated Ga (substitutional) on an Al grain boundary have been investigated by using a first-principles pseudopotential method. The segregated Ga is found to draw charge from the surrounding Al due to the electronegativity difference between Ga and Al, leading to a charge density reduction between Ga and Al as well as along the Al grain boundary. Such an effect can be enhanced by increasing the Ga segregation amount. With further Ga segregated, in addition to the charge-drawing effect that occurs in the Al–Ga interface, a heterogeneous α -Ga-like phase can form in the grain boundary, which greatly alters the boundary structure. These effects are suggested to be responsible for Ga-induced Al intergranular embrittlement.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

It is well known that impurity segregation in grain boundaries of metals can induce intergranular embrittlement. To understand the intergranular embrittlement, many computational attempts have been made. Effects of a segregated impurity on a grain boundary can be investigated based on atomic and electronic structures calculated from a first-principles method (see, for example, [1–5]). To determine whether a segregating impurity element is an embrittler or a cohesion enhancer, one can calculate the segregation energy difference of the impurity in a grain boundary and a fractured free surface based on the Rice–Wang model [6], which has been applied to different kinds of impurities in Fe and Ni grain boundaries [7]. Very recently, a first-principles computational tensile test was applied on a Ni grain boundary with S [8] and an

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Al grain boundary with Na or Ca [9], so as to reveal the intergranular embrittlement mechanism according to the tensile strength of the grain boundary with the segregated impurities.

Ga is an extreme example of an Al grain boundary embrittler. Experimentally, it has been found that a large amount of Ga penetrates Al polycrystals, causing intergranular brittle fracture [10]. Several studies show the rapid [11–13] and invasion-like [14] Ga penetration into Al grain boundaries. In the Ga penetration process, grain boundary structure can be greatly changed [14, 15], resulting in a significant increase of boundary mobility [15]. Furthermore, in a recent study, it has been observed that the maximum load of the Al samples decreases with increasing amount of segregated Ga, characterized by exposure time of these Al samples to Ga [16]. The brittle surface area has been shown to increase with increasing amount of Ga [16]. Thus, the brittle fracture, which is intergranular [10, 16], will dominate the fracture process when a large amount of Ga penetrates in the Al boundary. The experiments provide us with the information that segregated Ga induces Al intergranular embrittlement, and such embrittlement should be associated with grain boundary weakening due to the Ga segregation.

Computationally, only a few studies have been targeted for understanding the Ga-induced Al intergranular embrittlement. A direct investigation [1, 2] has been made on the atomic structure and energetics of an Al grain boundary segregated by different numbers of Ga atoms in different sites from first principles, which indicates the existence of energetically favourable local ‘tight sites’ for Ga segregation. These ‘tight sites’ play an important role in the behaviour of the Ga-segregated Al grain boundary. In addition, the surface energies of Ga-covered Al (111), (100), and (110) surfaces have been calculated [17]. This seems to indirectly suggest the weak cohesion between segregated Ga layers in an Al grain boundary. Despite these efforts, the origin of the Ga-induced Al intergranular embrittlement is still not fully clarified, making our understanding of such intergranular embrittlement difficult.

In this paper, we employ a first-principles pseudopotential method to investigate effects of Ga segregation on an Al grain boundary. According to the calculated electronic and atomic structure of the Al grain boundary with different amounts of segregated Ga impurity, the mechanism for Ga-induced Al intergranular embrittlement is suggested.

2. Computational method

All of the calculations have been carried out by using VASP [18], based on the density functional theory with the local density approximation. The interaction between ions and electrons is described by ultrasoft pseudopotentials [19, 20]. The calculated equilibrium lattice parameters are 3.98 and 5.60 Å for fcc Al and GaAs, respectively, in good agreement with the corresponding experimental values of 4.05 and 5.65 Å. The plane-wave energy cut-off is 204 eV. The energy relaxation iterates until the forces on all the atoms are less than 10^{-3} eV Å⁻¹.

We construct an 84-atom supercell of an AlΣ9(22̄1)/[110] tilt grain boundary, as shown in figure 1, with *x*, *y* and *z* axes along [22̄1], [11̄4] and [110] directions and the corresponding lattice lengths of 28.685, 8.443 and 5.629 Å, respectively. The supercell is the same as in our previous reports [4, 5]. The charge density is determined on a real-space grid of 280 × 80 × 56 points, and 32 *k*-points in the Brillouin zone are used. In the [22̄1] direction, two symmetric grain boundaries are introduced to give the periodicity. The calculated fully relaxed configuration of the clean AlΣ9 grain boundary agrees well with the high resolution transmission electron microscopy observations [4, 21]. To realize the Ga segregation, the Al atoms in the grain boundaries are substituted by different number of Ga atoms, as shown in figure 1, corresponding to different local segregation amounts of Ga.

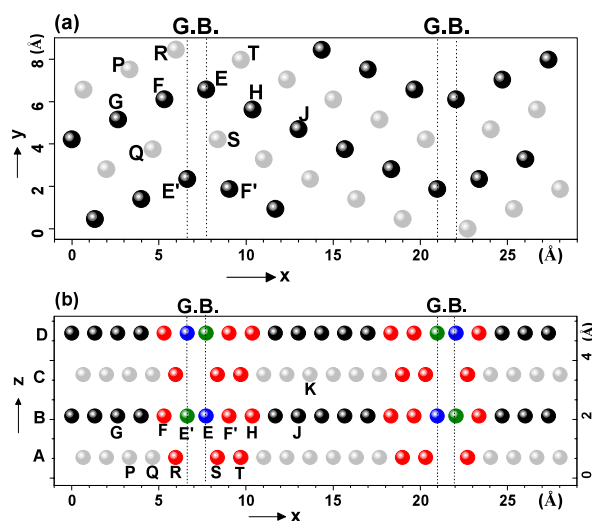


Figure 1. Supercell of an $\text{Al}\Sigma 9(221)/[110]$ tilt grain boundary. The supercell includes four (110) atomic layers. Layers C and D are equivalent to layers A and B, respectively, due to the double periods in the $[110]$ direction. (a) Top view of the supercell. Dark-grey and light-grey spheres indicate the atoms in the B (D) and A (C) layers, respectively. (b) Side view of the supercell. Four blue, four blue + four green and four blue + four green + 24 red spheres indicate, respectively, the substituted Ga atoms for Al in the four-, eight- and 32-atom substitution cases. Some atoms are marked for later discussion.

3. Results and discussion

We first calculated total energies of the supercell with one Ga atom substituted for one Al atom in the boundary (atom E in figure 1) and the bulk (atom K), respectively. The energy is shown to be lowered by ~ 0.2 eV due to the Ga segregation in the boundary in comparison with the bulk case, which indicates that Ga segregation in the Al boundary is energetically favourable. The tendency of Ga to segregate in the boundary interface or on the surface can be attributed to the larger cohesive energy of Al than Ga [17].

To investigate the effects of Ga segregation on the Al grain boundary as well as its dependence on the Ga segregation concentration, we perform the calculations of four-, eight- and 32-Ga-atom substitution cases (figure 1), respectively.

3.1. Four-Ga-atom substitution

The four-isolated-Ga-atom substitution is taken into account first (figure 1). Table 1 shows the interatomic distance between the atoms E and F and all their first nearest neighbours before and after the Ga segregation. EF and ER are interface reconstructed bonds. The interatomic distances show little change for the four-atom substitution case, as compared with those of the clean boundary, which implies that there is no obvious boundary volume or structure variation due to Ga segregation. This is different from the effect of other impurities such as Na, Ca or Si with the boundary either expanding or contracting [4]. The result is consistent with the fact that a Ga atom in a face-centred cubic (fcc) structure can exhibit nearly the same radius as an Al atom [1, 2], although its nearest neighbour radius is much smaller, as in α -Ga [22].

Given the almost unchanged boundary volume and structure after the Ga segregation, and taking into account that both Al and Ga own three valence electrons, it seems easy to

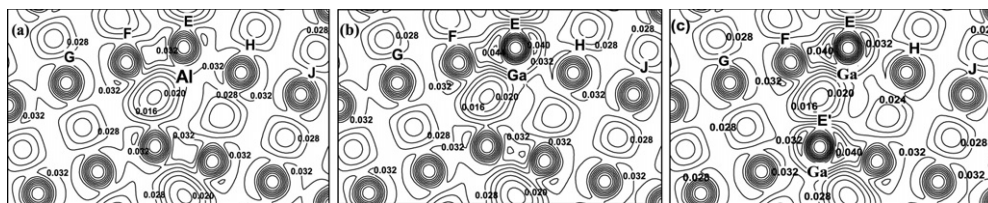


Figure 2. Contours of the valence charge density of the left half of layers B. (a), (b) and (c) represent the clean boundary and four- and eight-Ga-atom substitution cases, respectively. The interval of the contours is 0.004 au^{-3} . The atoms denoted by the letters E, F etc correspond to those in figure 1.

Table 1. The interatomic distance (\AA) between the atoms E and F and their first nearest neighbours. Al, Ga-4, Ga-8 and Ga-32 represent the clean boundary and four-, eight- and 32-Ga-atom substitution cases, respectively. Bold italic numbers indicate the Al–Ga atomic distances, while underlined numbers indicate the Ga–Ga distances.

	EF	ES	ET	EH	ER	FR	FG	FP	FQ
Al	2.621	2.811	2.727	2.761	2.828	2.971	2.800	2.777	2.741
Ga-4	2.592	2.810	2.720	2.760	2.839	2.955	2.825	2.792	2.740
Ga-8	2.586	2.806	2.724	2.763	2.843	2.946	2.804	2.782	2.736
Ga-32	<u>2.587</u>	<u>2.806</u>	<u>2.722</u>	<u>2.926</u>	<u>2.805</u>	3.049	2.780	2.793	2.726

speculate that there will be little change of the electronic structure as well. In contrast with our speculation, however, the grain boundary electronic structure is significantly altered by the Ga segregation. Figure 2(b) shows the charge density distribution for the four-atom case. Only the left halves of layer B are shown due to the supercell symmetry. In comparison with the clean boundary (figure 2(a)), the charge density accumulates around the Ga atoms, leading to a charge decrease between Ga atoms and the neighbouring Al atoms. This can be seen more clearly from figures 3(a) and (b), which show the charge density differences obtained by subtracting the charge density of the clean boundary from that of the Ga-segregated boundary for both layer B (with the segregated Ga atoms) and layer A (without Ga). Clearly, even in layer A, the charge density becomes lower along the boundary, though not continuous, indicating the significant effect of the Ga segregation on the electronic structure of the grain boundary.

The fact of the significant charge accumulation around the Ga atom and the charge depletion between the Ga and neighbouring Al atoms and also along the boundary implies that Ga draws charge from Al into itself. This is not surprising if considering the different electronegativity of Ga from Al. The electronegativity of Ga is 1.81 (Pauling electronegativity), and that of Al is 1.61 [23]. Ga has larger electronegativity than Al, leading to a charge drawing of Ga from Al in an Al–Ga interaction.

3.2. Eight-Ga-atom substitution

We further increase the amount of segregated Ga in the boundary to eight atoms (figure 1). The interatomic distances still exhibit little variation, similar to the four-atom case (table 1). However, as shown in figures 2(c), 3(c) and (d), further Ga segregation in the Al boundary induces further charge accumulation around the Ga atoms as compared with that of the four-atom case. This induces more significant charge reduction, and there forms a low charge density region that distributes continuously along the entire boundary. The results indicate that the charge drawing effect of Ga from Al is enhanced with increasing Ga segregation amount.

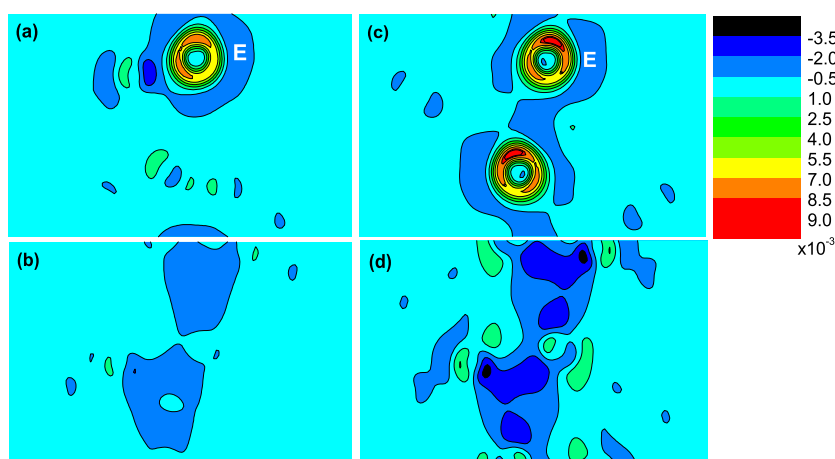


Figure 3. The valence charge density difference of the left half of layers B and A. (a) Layer B, four-Ga-atom substitution, (b) layer A, four-Ga-atom substitution, (c) layer B, eight-Ga-atom substitution, (d) layer A, eight-Ga-atom substitution. Positive indicates charge accumulation, while negative indicates charge depletion.

3.3. 32-Ga-atom substitution

Since the experiment shows that a large amount of Ga segregates in the Al grain boundary and Ga layers can be detected along the fresh fracture surface [10], we consider a more actual case that Ga forms a segregating layer in the boundary. In this case all the neighbouring Al atoms of the Ga atom E in the four- or eight-atom case are replaced by Ga so that a 32-Ga-atom segregating layer is formed (figure 1). The charge difference results for this case are shown in figure 4. It can be clearly seen that the charge density becomes much more localized at Ga. The results show that the segregated Ga atoms still draw charge from the surrounding Al, which makes the charge density much lower between Al–Ga and along the boundary. This is confirmed by the *yz*-planar integrated charge density profile shown in figure 5. But, as observed in the SiC/Al and SiC/Ti interfaces [24], the charge drawing from Al occurs only near the interface between the Al and Ga layers. The charge accumulation around the Ga atoms and the corresponding charge reduction between some Ga atoms inside the Ga segregating layer can be attributed to the formation of a heterogeneous phase, which significantly changes the grain boundary structure, as explained as follows.

Different from the four- and eight-atom cases, in which Ga atoms are relatively isolated, in the 32-atom case the Ga atoms interact with each other due to the formation of the segregating Ga layer in the boundary. It can be seen that bonds form between some Ga atoms, characterized by the higher charge density between these Ga atoms, such as between the Ga atoms of E and F (figure 4). On the other hand, the results of the interatomic distances (table 1) show the grain boundary structure has been altered, characterized by large bond length extensions of EH and FR as compared with those of the clean boundary. EH extends $\sim 6\%$ to 2.926 Å, while FR extends $\sim 3\%$ to 3.049 Å, in contrast with the four- and eight-atom cases, in which EH remains unchanged and FR contracts. The EF distance, which is 2.587 Å, is the shortest in comparison with all others, implying the formation of a stronger Ga–Ga bond between these two Ga atoms, consistent with the charge density analysis. The distances between other Ga–Ga atoms such as ES, ET, ER and EH are 0.14–0.34 Å longer as compared with EF. Thus, it can be readily considered that the grain boundary structure has been significantly altered by the segregation of

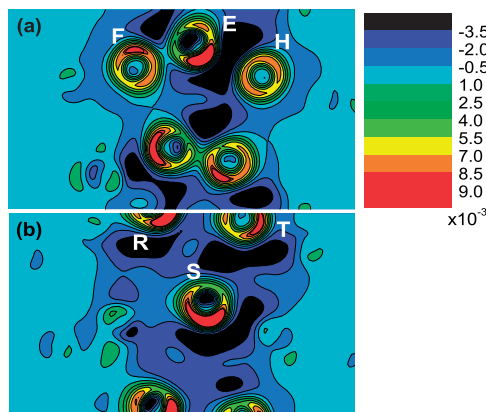


Figure 4. Valence charge density difference of the 32-Ga-atom substitution case. (a) The left half of layers B; (b) the left half of layers A. Positive indicates charge accumulation, while negative indicates charge depletion.

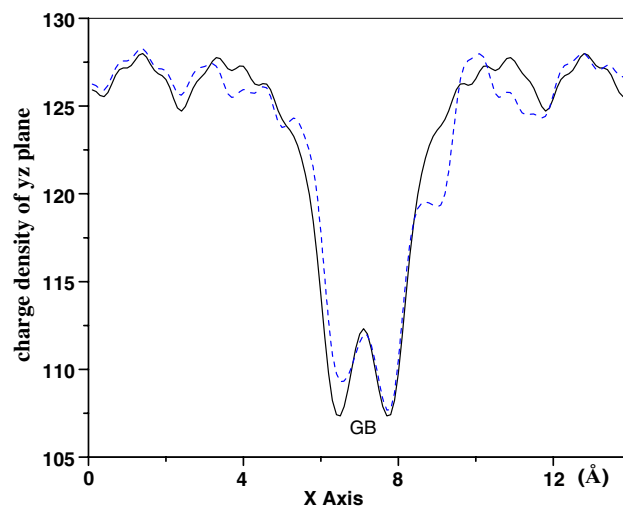


Figure 5. The yz-planar integrated charge density profile as a function of x coordinate. Solid black and dashed blue lines show, respectively, the clean boundary and the 32-Ga substitution case. The range of x coordinate of the Ga segregated layer is ~ 5.3 to 10.4 Å.

a large amount of Ga in the grain boundary. Ga forms a structure similar to α -Ga in the grain boundary (here we prefer to say it is like α -Ga rather than other phases of Ga (such as β -Ga) because α -Ga is the most stable of all the Ga phases), i.e. one shortest bond with the nearest neighbour Ga atom (a dimer-like bond) and several longer bonds with all other Ga atoms [22].

3.4. Ga-induced Al intergranular embrittlement

Now it is clear that Ga atoms draw charge from the surrounding Al atoms due to the electronegativity difference between Ga and Al, leading to the charge density decreases between Al and Ga and along the Al grain boundary. When the boundary is segregated by several Ga layers, besides the charge drawing effect that occurs in the Al–Ga interface, the grain

boundary structure alters greatly with the formation of a heterogeneous α -Ga-like structure. It is these effects that lead to the formation of many low charge density bonds in the boundary, which can be Al–Ga, Al–Al or Ga–Ga. These bonds can be weaker compared with the original Al–Al bonds without Ga segregation due to their lower charge density, causing the whole grain boundary to be weakened. Such weakened grain boundaries can be responsible for the Ga-induced Al grain boundary embrittlement, based on the consideration that these weakened boundaries can act as the origin of the crack and the preferential path of the crack under stress, resulting in the embrittlement. Such an embrittlement mechanism, which was first proposed by Losch [25], is also the case in several other systems, such as Fe/Ni–H [7, 26], Ni–S [8] and Al–Na/Ca [9].

The proposed Ga-induced Al intergranular embrittlement mechanism can well explain the experimental observations. With increasing Ga segregation amount, there form more low-charge-density bonds (Al–Al, Al–Ga or Ga–Ga) due to the charge drawing effect and the formation of the α -Ga-like structure. This may imply that the grain boundary can be further weakened with increasing Ga amount, and thus embrittlement can become more significant. This is consistent with the experimental observation that the maximum load of the Al samples decreases [16] and the embrittling effect (the brittle surface area) increases with increasing amount of Ga [10, 16]. Furthermore, when enough Ga segregates in the boundary, the boundary structure will be significantly altered; the grains can thus be separated by a heterogeneous phase that is α -Ga-like, causing a direct failure from the weakened grain boundary even without applied load, as observed in the experiment [10].

4. Conclusions

The atomic and electronic structure of an Al grain boundary with segregated Ga impurity atoms (substitutional) has been calculated by using a first-principles pseudopotential method. Ga is shown to draw charge from the surrounding Al, leading to a charge accumulation around Ga and a charge density decrease between Al–Ga and Al–Al, and also along the grain boundary. Such a charge-drawing effect can be enhanced by increasing the Ga segregation amount. Further segregation of Ga leads to the formation of a heterogeneous α -Ga-like structure, which alters the grain boundary structure greatly, causing a charge density reduction in both the Ga–Ga bonds and the Al–Ga interface. The charge density reduction can induce the grain boundary weakening and directly causes the intergranular embrittlement. As an extreme case, the heterogeneous α -Ga-like phase in the boundary will separate two grains, which can cause the experimentally observed direct intergranular failure.

Acknowledgments

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