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Vacancy diffusion in Cu $\Sigma = 9$ [110] twist grain boundary

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ABSTRACT

Both the formation energy and the diffusive activation energy of a single vacancy migrating in the first four atomic layers intra- and inter-layer near Cu $\Sigma = 9$ [110] twist GB have been investigated by using the MAEAM. The formation of the vacancy is favorable on the first layer (1L) near the GB plane and is spontaneous on sites '2'–'5' especially '2' and '4'. The effects of the GB on the intra- as well as inter-layer migration are mainly for 1L–1L as well as for 1L–1L′, 2L–1L and 3L–1L related to the 1L, respectively. Furthermore, the vacancy in 1L is favorable to migrate in 1L (intra-layer) or through GB plane to 1L′, the one in either 2L or 3L is favorable to migrate to 1L. So the vacancy tends to converge to the first layer near the GB plane.

1. Introduction

The diffusion of atoms on grain boundary (GB) plays an important role in many boundaries phenomena such as grain growth [1,2], impurity segregation [3], deformation [4] and fracture [5], etc. A number of experiments have been conducted to investigate the basic properties of GB, for instances, the mobility, diffusivity, and basic concepts like the Read–Shockley model of low angle boundaries [6] or the compensation effects [7,8] have been evolved from these results. Regardless of these achievements there is virtually no theoretical analysis of self-diffusion in GB to date.

In this paper, both the formation energy and the diffusive activation energy of a single vacancy migrating intra- and inter-layer in the first four atomic layers near Cu $\Sigma = 9$ [110] twist GB have been investigated by using the modified analytical embedded-atom method (MAEAM) developed by Zhang et al. [9–12] from analytical embedded-atom method (AEAM) of Johnson [13–16]. In our previous papers, the MAEAM has been used successfully to calculate the surface energy [17,18], the diffusive activation energy of the vacancy in the surface [19], the GB energy [20] and the interfaces energy [21].

2. Computational methods

In the MAEAM, the total energy of a system E_t is expressed as [22]

$$E_t = \sum_i F(\rho_i) + \frac{1}{2}\sum_i \sum_{j(\neq i)} \phi(r_{ij}) + \sum_i M(P_i) \quad (1)$$

$$\rho_i = \sum_{j(\neq i)} f(r_{ij}) \quad (2)$$

$$P_i = \sum_{j(\neq i)} f^2(r_{ij}) \quad (3)$$

where $F(\rho_i)$ is the energy to embed an atom in site i with electron density ρ_i, which is given by a linear superposition of the spherical averaged atomic electron density of other atoms $f(r_{ij})$, r_{ij} is the separation distance of atom j from atom i, $\phi(r_{ij})$ is the interaction potential between atoms i and j, and $M(P_i)$ is the modified term that describes the energy deviation from the linear superposition of atomic electronic density. The embedding function $F(\rho_i)$, pair potential $\phi(r_{ij})$, modified term $M(P_i)$ and atomic electron density $f(r_{ij})$ are taken as following forms [23–25]

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Table 1
The input physical parameters of Cu [24,25].

a (nm)	E_c (eV)	E_{1v}^f (eV)	C_{11} (eV nm^{-3})	C_{12} (eV nm^{-3})	C_{44} (eV nm^{-3})
0.36147	3.52	1.17	1050	760	470

$$F(\rho_i) = -F_0[1 - n\ln(\rho_i/\rho_e)](\rho_i/\rho_e)^n \tag{4}$$

$$\phi(r_{ij}) = k_0 + k_1(r_{ij}/r_{1e}) + k_2(r_{ij}/r_{1e})^2 + k_3(r_{ij}/r_{1e})^6 + k_4(r_{ij}/r_{1e})^{-12} + k_5(r_{ij}/r_{1e})^{-1} \tag{5}$$

$$M(P_i) = \alpha\left\{1 - \exp\left[-(\ln|P_i/P_e|)^2\right]\right\} \tag{6}$$

$$f(r_{ij}) = f_e(r_{1e}/r_{ij})^6 \tag{7}$$

where the subscript e indicates equilibrium state and r_{1e} is the first nearest neighbor distance at equilibrium. The cut-off distance of interaction potential for FCC metals r_{ce}, where the pair potential and its slope are zero, lies between the fifth and the sixth neighbor distances. That is, $r_{ce} = r_{5e} + k_{ce}(r_{6e} - r_{5e})$, in which k_{ce} is a model parameter needed to be fitted. F_0 and f_e can be calculated by [24]

$$F_0 = E_c - E_{1v}^f \tag{8}$$

$$f_e = \sqrt{E_c}/\Omega \tag{9}$$

where E_c is the cohesion energy corrected for the free-atom electron promotion and magnetic spin-polarization energies [26,27]. E_{1v}^f is the isolated vacancy formation energy, $\Omega = a^3/4$ is the atomic volume in FCC metals and a is the lattice constant. The remaining eight parameters (n, α, k_0, k_1, k_2, k_3, k_4 and k_5) used in Eqs. (4)–(6) are taken from Ref. [24]. The input physical parameters and the model parameters for Cu are listed in Tables 1 and 2, respectively. The interatomic potential for Cu is plotted in Fig. 1.

3. Computational and discussion

In an infinite twist GB, the coincident site lattice (CSL) can be generated by rotating one of the two adjacent grains about their common axis (taken as z axis here) until its lattice vector in its own coordinate becomes coincident with the vector of the un-rotating one. The reciprocal planar coincident density of crystal lattices (Σ) can be represented by the atom numbers in the smallest unit cell of CSL on each plane. The periodic boundary condition can be employed to reduce the number of atoms for representing the structure of the infinite twist GB. Fig. 2 shows the $\Sigma = 9$ [110] twist GB structure of the FCC metals and four identical smallest coincident unit cells. The x and y axes are attached to the un-rotating grain in which the atom sites on adjacent two (110) lattice planes are represented by open circles (the nine atoms in each unit cell of CSL are indicated by red numbers '1'–'9') and open squares (the nine atoms are indicated by blue letters 'a'–'i') for odd layer (2n − 1)L and even layer 2nL, respectively. Similarly, the x' and y' axes are selected to be attached to the rotating grain in which the atom sites on adjacent two (110) lattice planes are represented by open rhombuses (the nine atoms in each unit cell of CSL are indicated by orange letters 'a''–'i'') and open triangles (the nine atoms are indicated by black numbers '1''–'9'') for odd layer (2n − 1)L and even layer 2nL, respectively. The superscript '' implies the parameter in the rotating grain throughout the paper.

Due to the equivalence between the rotating and un-rotating grains, only the initial sites of a single vacancy in different layers of the un-rotating grain should be considered. Furthermore, as can be seen easily from Fig. 2, only the vacancy sited initially at five positions such as the red numbers '1'–'5' for the odd layers or blue letters 'a'–'e' for the even layers should be considered, since the smallest unit cell of CSL has a twofold rotating axis paralleled z axis through its center 'a' as well as 'a'' and thus the sites '6', 7', '8' and '9' are equivalent to '5', '4', '3' and '2' or 'f', 'g', 'h' and 'i' are equivalent to 'e', 'd', 'c' and 'b', respectively. A super-cell with eighty (110) layers is used in computation for each grain, which consists of a computational cell of free atoms surrounded by a mantle of atoms fixed at their perfect lattice positions. Twenty times periodic lengths $\sqrt{2}a/2 \times a \times \sqrt{2}a/4$ in $x \times y \times z$, that is $10\sqrt{2}a \times 20a \times 5\sqrt{2}a$, is chosen as the computational cell for each grain, where a is the lattice constant. A vacancy in different layers is created by removing an atom from corresponding layer. The formation energy of the isolated vacancy E_{1v}^f can be calculated by [28]

$$E_{1v}^f = E(N-1) - E(N) + E_c \tag{10}$$

where $E(N-1)$ is the energy of the computational cell containing $N-1$ atoms and a single vacancy, $E(N)$ the energy of the perfect computational cell containing N atoms but without any vacancies and E_c is the corrected cohesion energy and compensates for the missing atom [28]. The diffusion activation energy Q_v of the vacancy is obtained by

$$Q_v = E_{sad} - E_{eq} + E_{1v}^f \tag{11}$$

where E_{sad} and E_{eq} stand for the system energy with the vacancy in the saddle point potential energy configuration and at initial equilibrium position, respectively.

The calculated formation energies E_{1v}^f of a single vacancy in five sites of the first four layers near the GB plane are listed in Table 3. The negative formation energies of the vacancy on sites '2'–'5' of the 1L mean that the formation of the vacancy on these sites is spontaneous especially on sites '2' and '4'. This is because, as can be seen in Fig. 2, in addition to the effects of the other nearest neighbor atoms, the distance between the atoms at sites 'e'', 'c'', 'b'' and 'd'' (open rhombuses and orange letters) on the 1L′ of rotating grain and the atoms at sites '3', '5', '4' and '2', respectively, decreases successively and thus increasing in the repulsive force and decreasing in the vacancy formation energy successively. For example, as can be seen in Fig. 1, the largest negative formation energy of −70.72 eV for the vacancy formed on site '2' is resulted from the shortest distance (r/r_{1e}) of 0.58 between the original atom 2 on the 1L and the atom d′ on the 1L′ and thus the largest repulsive energy of 74.59 eV. On the coincident site '1' of the 1L only 1.14 eV energy is needed. In the 2L, the lowest formation energy of 1.15 eV on centric coincident site 'a' is slightly higher than the highest one of 1.14 eV on coincident site '1' of the 1L, and the formation energy of 1.19 eV on site 'b', 'c' or 'd' is the highest in all the values, and the value of 1.17 eV on site 'e' is equal to the one on coincident site '1' of

Table 2
The model parameters of Cu for MAEAM [24].

n	α (eV)	k_{-1} (eV)	k_0 (eV)	k_1 (eV)	k_2 (eV)	k_3 (eV)	k_4 (eV)
0.60	0.003163	1.499487	−0.650171	0.097645	−0.00006	0.098837	−1.178326