Validity of Activation Energy for Vacancy Migration Obtained by Integrating Force–Distance Curve

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Kuramoto *et al.* calculated the activation energy for dislocation loop migration by integrating the force–distance curve. Their method has a great potential for the determination of migration energy in many cases. However, the validity of the application of their method to point defect migration has not yet been proved, because the migration of point defects is a thermally activated process and the physical meaning of the force in the force–distance curve has not been clarified. In this study, the validity was investigated by three methods to calculate the vacancy migration energy. In the first method, the migration energy was obtained by definition from the difference in potential energy between the equilibrium configuration before migration and the saddle point configuration (Method 1) using a statistic lattice relaxation method. The second method involved a molecular dynamics simulation based on an absolute reaction rate theory (Method 2). The third method involved the integration of the force–distance curve obtained by the statistic lattice relaxation method mentioned above (Method 3). The calculation model used was a two-dimensional hexagonal lattice and the Morse potential for Cu was used. The migration energies obtained by Methods 1, 2 and 3 were 0.391 eV, 0.394 ± 0.009 eV and 0.392 eV, respectively. As these values were similar, the validity of Method 3 was demonstrated.

[doi:10.2320/matertrans.MAW200714]

(Received April 23, 2007; Accepted June 12, 2007; Published August 1, 2007)

Keywords: vacancy, migration energy, molecular dynamics, statistic method

1. Introduction

Point defects play the main role in the migration of atoms in most solids. Therefore, the activation energy for point defect migration, E_m , is one of the important material parameters in solids and is defined by the difference in potential energy between the equilibrium configuration (lowest energy state) and the saddle point configuration (highest energy state). An example of a moving atom adjacent to a vacancy is shown in Fig. 1. At the saddle point configuration, the potential energy is highest between two equivalent positions. By calculating the energy difference between the equilibrium configuration and the saddle point configuration, the migration energy can be obtained (Method 1).^{1–4)}

As the jump rate of vacancies is proportional to $\exp(-E_m/kT)$, the migration energy is also obtained using the temperature dependence of the number of point defect jumps by molecular dynamics simulation (Method 2). Here, T is the absolute temperature and k is the Boltzmann constant. There were several works on the calculation of the migration energy of interstitial clusters in Fe using molecular dynamics.^{5–8)} The activation energy for the motion of interstitial clusters was approximately 0.06 eV; it was almost constant or slightly decreased with an increase in the size of the clusters (less than 20 clusters).

Kuramoto *et al.* obtained the migration energies of interstitial type dislocation loops (bundled crowdions) by integrating the force–distance curve.^{9,10)} The migration energy obtained by this method in Fe was similar to that obtained using the molecular dynamics mentioned above. A $\tau bl - d$ curve was obtained from the result of the stepwise stressing of a dislocation loop. Here, τ is the shear stress applied to the loop, τb is the force acting on the unit length of the loop, l is the total circumference of the loop and d is the

Fig. 1 Diagram of vacancy migration. Atoms around vacancies prevent the movement of the gray atom (vacancy migration). The vacancy migration energy is defined as the energy difference between an initial equilibrium state and a saddle point state. The jump rate of vacancies is proportional to $\exp(-E_m/kT)$.

distance moved. The migration energy was obtained by integrating τbl from the initial equilibrium point to the saddle point.

Sato *et al.* obtained the migration energy of point defects by the same method (Method 3).¹¹⁾ However, in their case, the physical meaning of the force required to move a point defect has not been clarified, because point defects migrate in a thermally activated process, i.e., point defects with energies higher than the migration energy can jump to the neighboring sites, and actually, no force acts on them. Therefore, the validity of the force–distance curve method for obtaining the point defect migration energy has not been confirmed. In the case of dislocation loops, the shear stress is the Peierls stress and the force is a physical quantity.

To prove the validity of the force–distance curve method for obtaining the activation energy for vacancy migration, three calculation methods (Methods 1–3) were compared in this study.

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Fig. 2 Vacancy migration by applying force to gray atom. With the atomic displacement, the force applied to the gray atom was calculated at each point. The vacancy migration energy was obtained by integrating the force–distance curve $E_m = \sum F \Delta d$.

2. Calculation Method

A two-dimensional hexagonal lattice was chosen for the calculation of the vacancy migration energy, since a long time is required for the molecular dynamics simulation of vacancy migration at low temperatures. At high temperatures, lattice instability occurs. The model lattices were $20a \times 10\sqrt{3}a$ (a : atomic distance, 400 atoms) and $10a \times 5\sqrt{3}a$ (100 atoms), and a fixed boundary condition (one layer on the surface) and a periodic boundary condition (parallel to the surface) were used for the statistic lattice relaxation methods (Methods 1 and 3) and molecular dynamics simulation (Method 2), respectively. In these calculations, the Morse potential for Cu^{12–14)} was used.

Three methods of obtaining the vacancy migration energy were used as mentioned in Introduction. In Method 1, the vacancy migration energy was obtained as the energy difference between an initial equilibrium position and a saddle point, as shown in Fig. 1. All atoms except for boundary atoms were fully relaxed to obtain the initial equilibrium state. On the other hand, in order to obtain the energy at the saddle point, the gray atom in Fig. 1 and boundary atoms were fixed and other atoms were fully relaxed. The lattice energy was obtained by the statistic lattice relaxation methods and all the results obtained correspond to $T = 0$ K.

In Method 2, constant-NVE (number of atoms, volume and energy) molecular dynamics and a modified velocity-Verlet algorithm with a time step of 1 fs were used. The number of vacancy jumps was calculated to be 10^6 MD time steps at five temperatures. The vacancy migration energy was derived from the relation between the number of vacancy jumps and the temperatures. In Method 3, the migration path of the gray atom in Fig. 2 to the saddle point was divided into 20 equal points. The gray atom was moved in order, and at each point, all atoms except for the gray atom and boundary atoms were fully relaxed, and the force applied to the gray atom was calculated. The vacancy migration energy was obtained as $E_m = \sum F \Delta d$ in Fig. 2, where F is the force applied to the gray atom at each point and Δd is the infinitesimal distance.

3. Results and Discussion

Table 1 shows the total energy of the model lattice with the initial equilibrium state and saddle point. The vacancy migration energy obtained by Method 1 was 0.391 eV.

Table 1 Total energy of model lattice with initial equilibrium state and saddle point.

Total energy of model lattice, E/eV	
Initial equilibrium state	–484.241
Saddle point	–483.850

Table 2 Numbers of vacancy jumps at 483.98 K, 601.27 K, 703.72 K, 824.16 K and 880.24 K obtained using constant-NVE molecular dynamics.

Temperature, T/K	Number of vacancy jumps	Standard deviation
483.98	2.86	1.91
601.27	19.14	4.89
703.72	56.93	7.89
824.16	143.86	13.39
880.24	200.97	15.26

Fig. 3 Relation between number of vacancy jumps and inverse temperature (Arrhenius plot). The line was obtained by least-squares analysis.

In MD simulation (Method 2), 10^6 MD time step calculation was repeated 100 times. In each repetition, the initial atomic positions and momentums were set to be the same as those calculated in the prior step. The numbers of vacancy jumps obtained by 100 times of calculations were averaged. The obtained temperatures were also averaged, since temperature was not controlled in the simulation. The numbers of vacancy jumps at 483.98 K, 601.27 K, 703.72 K, 824.16 K and 880.24 K are shown in Table 2. At high temperatures, the number of vacancy jumps was high during the 10^6 MD time step calculation. However, the model lattice was not stable and the number of vacancy jumps was not reliable. At low temperatures, the number of vacancy jumps was low and the standard deviation of the number of vacancy jumps was large. Therefore, we selected five temperatures in an appropriate temperature range. Figure 3 shows the relation between the number of vacancy jumps and the inverse temperature (Arrhenius plot). The vacancy migration energy obtained from the slope of a line analyzed by a least-squares method was 0.394 ± 0.009 eV.

The migration energy was obtained at a constant volume, i.e., the volume of the model lattice was determined when the total energy of the model lattice was minimum at 0 K and the volume was kept constant independently of temperature. Sato and coworkers reported that the formation and migration energies of vacancies change up to 7% at an elastic strain of

Fig. 4 Force–distance curve obtained by statistic lattice relaxation method. The migration path from the initial equilibrium state to the saddle point was divided into 20 equal points. At each point, the force applied to the atom was calculated. The vacancy migration energy was obtained as $E_m = \sum F \Delta d$.

1%.^{1,2)} The volume change induced by thermal expansion or introducing vacancies is very small compared with that induced by the 1% elastic strain. Moreover, the directions of these volume changes are opposite, thereby canceling each other. Therefore, the effect of a volume change can be neglected.

Figure 4 shows the force–distance curve obtained by Method 3. The normalized distance was obtained by dividing the actual distance by the atomic distance a . We obtained a vacancy migration energy of 0.392 eV by integrating the force–distance curve.

The vacancy migration energies obtained by Methods 1 and 2 were reliable, because they were based on the definition of the vacancy migration energy and the absolute reaction rates, respectively. The vacancy migration energy obtained by Method 3 was similar to those obtained by the other two methods. Therefore, the validity of the vacancy migration energy obtained by integrating the force–distance curve was demonstrated.

In this study, we employed a two-dimensional system. However, the obtained result is applicable to a three-

dimensional system. The existence of a saddle point for vacancy migration is essential for these calculations, and there exists a saddle point even at a two-dimensional hexagonal lattice, as shown in Fig. 4. Therefore, no problems exist to extend the validity of the method of integrating the force–distance curve to a three-dimensional system.

4. Conclusion

The vacancy migration energy was calculated by two statistic lattice relaxation methods and molecular dynamics simulation in a two-dimensional hexagonal lattice. The obtained values were approximately 0.39 eV in the three methods. The validity of the vacancy migration energy obtained by integrating the force–distance curve was demonstrated. This method is expected to be effective in obtaining the migration energies of point defects when the saddle point configuration is not easily determined.

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