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Three-dimensional Ehrlich-Schwoebel Barriers of W

Z. Xu[1], L. G. Zhou[1], Jian Wang[1], Timothy S. Cale[2] and Hanchen Huang[1,3]

Abstract: Recent studies show that three-dimensional Ehrlich-Schwoebel (3D ES), or facet-facet, barriers of face-centered-cubic metals are substantially higher than other surface diffusion barriers. This paper presents the numerical results of 3D ES barriers for body-centered-cubic W, using classical molecular statics calculations and the nudged elastic band method. Results show that an adatom on W$\{110\}$ has a diffusion barrier of 0.49 eV on the flat surface, 0.66 eV over a monolayer step, and 0.98 eV over a ridge to a neighboring $\{100\}$ facet, which is one 3D ES barrier.

keyword: BCC, W, Diffusion barrier, Ehrlich-Schwoebel

1 Introduction

Diffusion barriers are one of the most crucial factors in thin film deposition processes [Ohring (1992)]. In general, diffusion barriers on a flat surface, down a monolayer step, and down a multiple-layer step are controlling factors during surface processing. When diffusion barriers are large, mass transport is difficult and film surfaces tend to be rough. For polycrystalline thin films, an effective diffusion barrier is commonly quoted to describe mass transport over surfaces of various crystal orientations. On different crystal surfaces of a polycrystalline film, the diffusion barriers are different. Further, on each surface, there are several diffusion barriers, for example the diffusion barrier of an adatom on a flat surface, that down a monolayer step, and that down a multiple-layer step. Most studies have focused on diffusion on flat surfaces. The diffusion barrier for atomic motion down a monolayer step on an otherwise flat surface can be larger than that on a flat surface. The extra barrier is called an Ehrlich-Schwoebel (ES) barrier [Ehrlich and Hudda (1966); Schwoebel and Shipsey (1966)]; As shown in Figure 1, in this work we use the term two-dimensional (2D) ES barrier for the total diffusion barrier over a monolayer step. In contrast, the diffusion barrier down a multiple-layer step is named three-dimensional Ehrlich-Schwoebel (3D ES) barrier or facet-facet barrier.

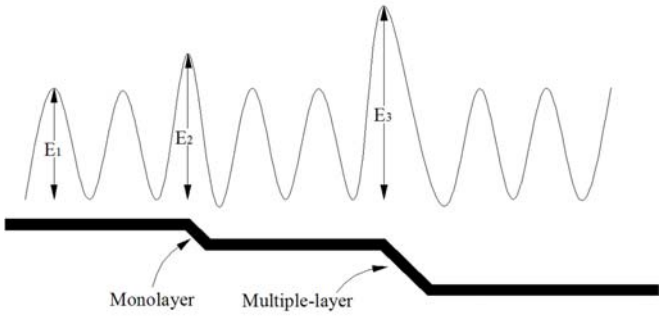


Figure 1 : Schematics showing atomic diffusion barrier on a flat surface (E_1), that down a monolayer step (E_2), and that over a multiple-layer step (E_3).

Recently, Huang and co-workers reported that 3D ES barriers can be larger than 2D ES barriers for face-centered-cubic (FCC) Al and Cu [Liu et al. (2002); Huang et al. (2002)]. Experiments on Cu [Huang et al. (2003)] and Ag [Tang et al. (2002)] indirectly confirm the larger magnitude of the 3D ES barrier. Further, the 3D ES barrier of dimers is even larger than that of adatoms [Coronado and Huang (2005)].

The 3D ES barrier becomes important once micro-facets are next to each other. Such micro-facets are populous on film surfaces and exist for not only FCC metals but also body-centered-cubic (BCC) metals. In particular, BCC W has applications in the form of thin films, preferably with low surface roughness [Aouadi and Parsons (1992)]. Surface diffusion, or its anisotropy, can lead to nanostructure formation on W$\{100\}$ surfaces [Singh et al. (2003)]. In this paper, we investigate the 3D ES barriers of W involving high symmetry surfaces $\{100\}$ and $\{100\}$.

[1] Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180
[2] Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180
[3] Correspondence author, email: hanchen@rpi.edu

2 Method

This investigation relies on the classical molecular statics method, and the nudged elastic band method [Jonsson et al. (1998)]. The following presentation focuses on two elements of the calculation method: (1) the interatomic potential used, and (2) setup of the simulation cell.

The interatomic potential, which prescribes how W atoms interact with each other, is a critical element of molecular statics calculations. The many-body Ackland potential [Ackland and Thetford (1987)] for W gives a reasonable vacancy formation energy of 3.71 eV [Matthai and Bacon (1985)], when compared with the first principles result of 3.27 eV [Korhonen et al. (1995)] and to the experimental values of 3.6-4.1 eV [Schultz and Ehrhart (1991)]. More importantly, this potential gives surface formation energies of 2.570 J/m^2 for $\{100\}$, in comparison to the 2.800 J/m^2 from experiments [Bettler and Barnes (1968)]. We have also used this potential in the simulation of thin film deposition [Liu et al. (2002)]. Due to its reliability in describing point defect and surface formation energies, the Ackland potential is chosen to describe the interatomic interactions of W.

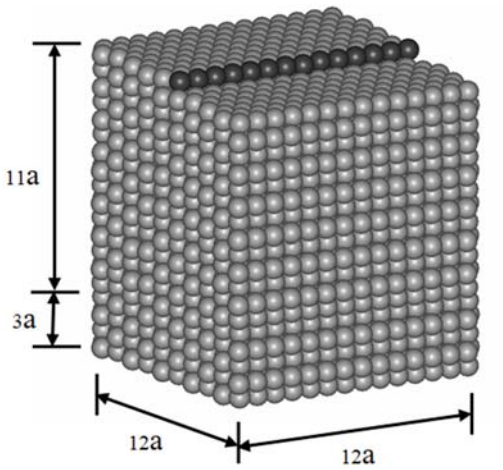


Figure 2 : Simulation cell with dimensions labeled in unit of lattice constant a.

The W atoms in the simulation cell occupy a BCC crystal lattice, as shown in Figure 2. Periodic boundary conditions are applied along the two horizontal directions. Along the vertical direction, no periodic boundary condition applies. A region at the bottom of the cell of about 3a in thickness is fixed to mimic a semi-infinite bulk region. The top region represents various surface configurations. On the top surface, steps of various thicknesses along various directions are created by removing atoms; shown in Figure 2 is a monolayer step. When the steps are multiple-layer in thickness, they are micro-facets. Neighboring $\{100\}$ facets (hexagons) and $\{100\}$ facets (squares) are shown in the Wulff construction of Figure 3.

In determining the diffusion barriers of adatoms across neighboring micro-facets, the nudged elastic band method [Jonsson et al. (1998)] ensures a continuous migration path. In this method, a series of atomic configurations [R_0, R_1,...,R_N] are constructed to represent a initial path, where R_0 and R_N represents the initial and final positions of all atoms, respectively. The initial path converges to the minimum energy path with intermediate configurations adjusted by optimization. The path continuity is ensured by the spring interaction between adjacent configurations. Then the intermediate configurations relax so the energy converges to a minimum through iteration. The saddle points on the potential surface are identifiable as the maxima on the converged energy path. The convergence of numerical results is tested by using different simulation cell sizes.

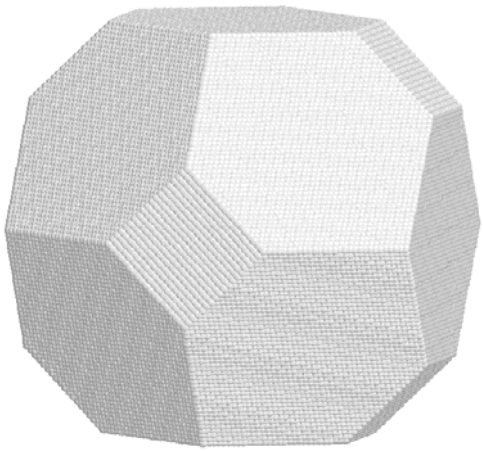
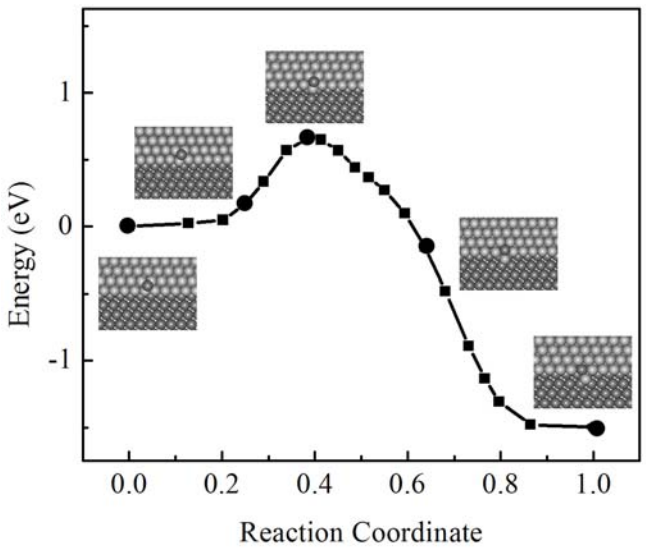


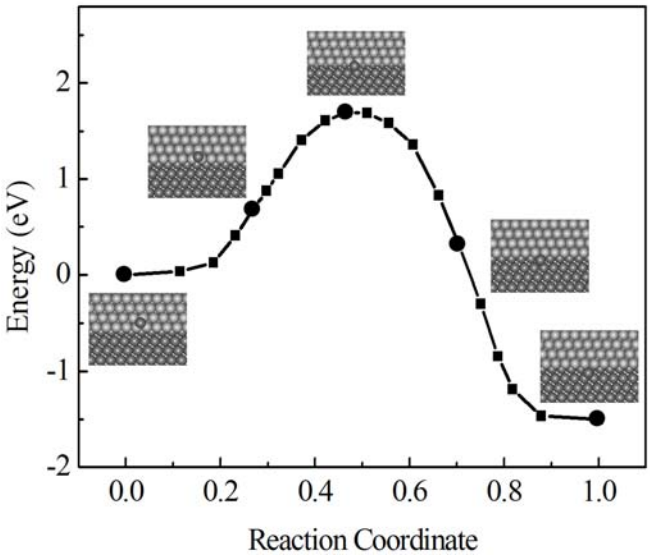
Figure 3 : The Wulff construction of W, according the surface formation energies given by the Ackland potential.

3 Results

In this section, we first present the diffusion processes between neighboring facets in detail, and then summarize the numerical results in two tables. On a $\{100\}$ surface, an adatom may diffuse down two different steps.



(a)



(b)

Figure 4 : (a): Energy profile of adatom diffusing down a monolayer $< 111 >/\{100\}$ step through exchange. Atomic configurations corresponding to the circular points on the curve are included as insets. (b): Energy profile of adatom diffusing down a monolayer $< 111 >/\{100\}$ step through direct hopping. Atomic configurations corresponding to the circular points on the curve are included as insets.

Each step is labeled by its direction and the plane of its side facet. For example $< 111 >/\{100\}$ represents a step

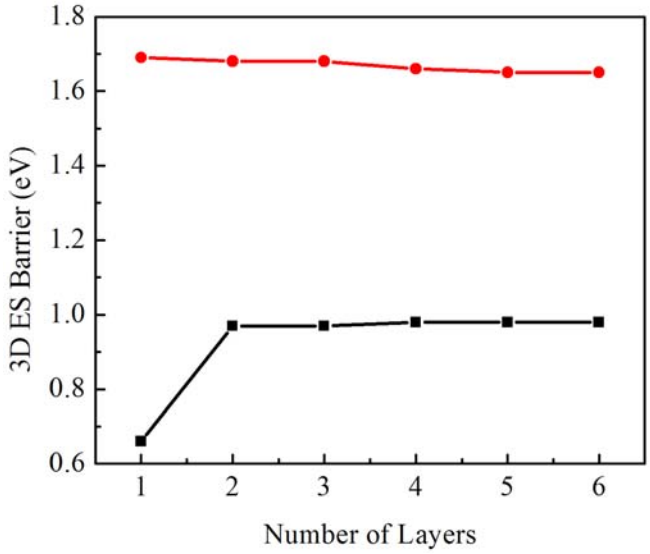


Figure 5 : Diffusion barrier as a function of step thickness, according to exchange mechanism (squares) and direct hopping (circles).

along the $< 111 >$ direction with side facet being $\{100\}$. The energy profiles of an adatom diffusing down a monolayer $< 111 >/\{100\}$ step are presented in Figure 4 for both exchange and hopping mechanisms. The exchange mechanism is preferable because of the correspondingly smaller diffusion barrier. Compared to the diffusion barrier of 0.49 eV on a $\{100\}$ surface, the extra barrier an adatom experiences is 0.17 eV. This compares reasonably well with the experimental value of 0.20 eV reported by Wang and Tsong (1982).

As the monolayer step becomes a facet, the diffusion barrier changes from a 2D ES barrier to a 3D ES barrier. Figure 5 shows this transition for diffusion between two $\{100\}$ facets ($< 111 >/\{100\}$), which are thermodynamically preferred. According to the exchange mechanism, the transition from 2D ES barrier to 3D ES barrier starts at two layers (0.97 eV) and completes at four layers (0.98 eV). The 2D ES barrier is only 0.66 eV, in contrast to 0.98 eV for the 3D ES barrier.

Tables 1 and 2 summarize the numerical values of diffusion barriers as a function of step thickness (in units of number of layers) for various step orientations and facets. For diffusion between $\{100\}$ and $\{100\}$ facets, the barrier decreases by a small amount (0.06 eV) as the step goes from one layer to two layers in thickness, and then it remains independent of the step thickness.

Table 1 : Diffusion barriers (eV) for W with exchange mechanism

Initial Facet	Step Orientation/ Final Facet	Number of Layers					
		1	2	3	4	5	6
$\{100\}$	$< 111 >/\{100\}$	0.66	0.97	0.97	0.98	0.98	0.98
	$< 100 >/\{100\}$	0.88	0.82	0.82	0.82	0.82	0.82
$\{100\}$	$< 100 >/\{100\}$	2.45	2.34	2.34	2.34	2.34	2.34

Table 2 : Diffusion barriers (eV) for W with hopping mechanism

Initial Facet	Step Orientation/ Final Facet	Number of Layers					
		1	2	3	4	5	6
$\{100\}$	$< 111 >/\{100\}$	1.69	1.68	1.68	1.66	1.65	1.65
	$< 100 >/\{100\}$	0.88	0.90	0.92	0.92	0.92	0.93
$\{100\}$	$< 100 >/\{100\}$	2.54	2.50	2.49	2.49	2.49	2.49

It is interesting to discuss impacts of the numerical results before closing. Since copper has been studied in some detail in terms of its diffusion barriers and characterization of surface dimensions [Wang et al. (2004)], we use it as a reference in this discussion. The difference between the smallest 3D ES barrier and the diffusion barrier on flat surface of Cu$\{111\}$ is 0.26 eV, or 2.3 in the unit of kT_m; k is the Boltzmann constant and T_m the melting temperature, 1358 K for Cu [Kaye and Laby (1948)]. The counterpart of Cu$\{111\}$, thermodynamically the most stable surface, is $\{100\}$ in W. In the W, this barrier difference is 0.49 eV, or 1.6 in the unit of kT_m; the melting temperature is 3660 K for W [Kaye and Laby (1948)]. At one quarter of the melting temperature, the extra barrier reduces surface diffusion coefficient by 600 times in W, and 10000 times in Cu. The reduction in W is smaller, but still substantial.

4 Conclusions

We have determined the 3D ES barriers of BCC W. Our calculations show that, on the thermodynamically most stable surface $\{100\}$, an adatom has a diffusion barrier of 0.49 eV on the flat surface, of 0.66 eV down a monolayer $< 111 >$ step, and of 0.98 eV over a ridge to another $\{100\}$ facet. Like in FCC Cu, this 3D ES barrier of 0.98 eV will be the determining factor of W surface facet dimensions.

For reference, our calculations also extend to thermodynamically less preferred $\{100\}$ surfaces. The diffusion from $\{100\}$ to a neighboring $\{100\}$, whether a monolayer step or multiple-layer step, is above 0.8 eV and much larger than the 0.49 eV on a flat $\{100\}$ surface.

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