not much greater than migration energies, the data indicate relatively small binding energies of clusters rather than the large binding energies reported. For instance, Ehrlich and Hudda[2] report the migration energy of W adatoms on a W $\{110\}$ surface as 0.96 eV and Tsong finds that W di-clusters dissociate with an energy of 1.02 eV. This yields a binding energy for W di-clusters on a W $\{110\}$ surface of 0.06 eV. Reasonably large error limits must be associated with the 1.02-eV dissociation energy, but clearly the di-clusters are weakly bound.

SUMMARY

From the data given by Tsong[1] and standard kinetic analysis, the activation energy for migration of Re adatoms on a $\{110\}$ W surface at 364 °K is approximately 1.00 eV with the saddle point being at c sites, independent of whether a or b sites are most stable. The greatest uncertainty arises from imprecise knowledge of the effective frequency factor ν. Bassett and Parsley[5] obtained 1.04 eV for the same quantity, although the details of their data were not given.

The data at lower temperatures are inconsistent with the analysis at 364 °K, however. Of many possible explanations, the authors prefer one involving an activation energy which is monotonic increasing with the temperature, at least within the temperature range investigated.

The data given by Tsong[1] for Re-Re, Re-W, and W-W clustering on W surfaces indicate that the binding energies are small relative to the migration energy of either Re or W adatoms.

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Surface Diffusion and Cluster Binding Energy of Individual Atoms on Tungsten Surfaces*

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Some of the field-ion-microscopy data reported earlier are reinterpreted according to the comments given by Johnson and White. Their comments are either clarified or extended. The surprising result of the new interpretation is the exceedingly low binding energies of clusters.

INTRODUCTION

Recently we reported an experimental investigation of interactions between individual atoms on tungsten surfaces.[1] Attempts were made to analyze the surface-diffusion data obtained on W $\{110\}$ planes by assuming that the atomic migrations follow the two-dimensional surface channels of the substrate plane. The binding energy of an atom in a cluster was investigated by observing the temperature at which the cluster dissociates within a heating cycle of 145 sec. As pointed out by Johnson and White,[2] some effects were not properly taken into account in our analysis. We therefore present here some new interpretations of our data. This also serves to clarify or extend their comments.

DIFFUSION ANALYSIS

We will follow the notations of Johnson and White. As pointed out by them, in our analysis, a continuous sequence of $b \to a \to b$ jumps was allowed. On W $\{110\}$ planes, this is not so, and the activation energies obtained are, therefore, not correct. This does not mean, however, that the method used is wrong. To substantiate this point, let us assume that a sites are the stable sites and also $E_b \ll E_c$. As shown in Fig. 1, for each a site, there are four nearest a sites with their coordinates given by

$$\begin{array}{ll} x_1 = -a, & y_1 = \sqrt{2}\, a \\ x_2 = a, & y_2 = \sqrt{2}\, a \\ x_3 = -a, & y_3 = -\sqrt{2}\, a \\ x_4 = a, & y_4 = -\sqrt{2}\, a \end{array} \qquad (1)$$

where a denotes the lattice constant. The effective jumping frequencies to all neighbor a sites are equal and are given by

$$\nu_1 = \nu_2 = \nu_3 = \nu_4 = \tfrac{1}{4} kT/h \; e^{-E_c/kT}. \qquad (2)$$

Thus,

$$\langle(\Delta x)^2\rangle=\tau\sum_{j=1}^{4}\nu_j x_j^2=\tau a^2(kT/h)e^{-E_c/kT},$$
$$\langle(\Delta y)^2\rangle=\tau\sum_{j=1}^{4}\nu_j y_j^2=2\tau a^2(kT/h)e^{-E_c/kT}. \tag{3}$$

This result agrees with that of Johnson and White. When instead b sites are the stable ones, but $E_a \ll E_c$, the mean-square displacements are still given by Eq. (3). This can be visualized by considering a limiting case where $E_a \to E_b$. There will be no distinction between a and b sites. The two modes of diffusion should then give the same result. Johnson and White, on the other hand, give a factor of two difference in the two cases. The important thing here is that both modes of diffusion give a ratio $\langle(\Delta y)^2\rangle/\langle(\Delta x)^2\rangle=2$, which agrees within 5% with the 2.09 ratio obtained for a rhenium atom diffusing on a W $\{110\}$ plane at 364 °K. There is indeed no *a priori* way to decide from this experiment which of the two modes is actually occurring. If one assumes that the interatomic potentials between metal atoms are spherically symmetric, a sites are then saddle points. They cannot be the stable sites. Within the assumption, one can conclude that the surface sites (b sites) are the stable ones. The activation energy of surface diffusion for Re atoms on W $\{110\}$ planes is then given by $E_c=1.01$ eV.

DIFFUSION KINETICS

Using the data shown in Fig. 2 of Ref. 1, Johnson and White conclude that the activation energy of surface diffusion of rhenium atoms on W $\{110\}$ planes is given by $E_c=1.33\times10^{-3}(T+380)$ eV. Figure 2 of Ref. 1 was intended to show the existence of potential traps on surfaces. It is also implicitly understood that when adatoms are continuously trapped or interactions are present among adatoms, the mean-square displacements obtained are not accurate, and should not be used for calculating the activation energy of surface diffusion. Investigations by Ehrlich and Hudda,[3] and by Brenner[4] with perfect planes over wide temperature ranges show that activation energy is constant.

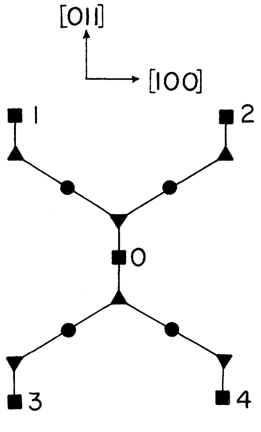

FIG. 1. Unit surface channel on a W {110} plane. The symbols are adapted from Ref. 2. Each a site is surrounded by four nearest-neighbor a sites.

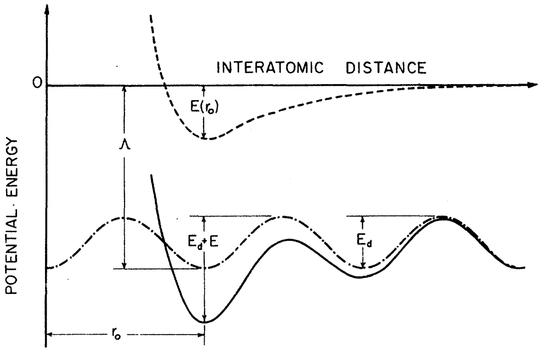

FIG. 2. Schematic diagram showing the relationship among various potentials. Λ denotes the binding energy of an adatom on the crystal plane, E_d is the activation energy of surface diffusion of a single atom, and $E(r)$ is the interatomic potential energy between two adatoms.

It is appropriate to point out here that the potential trap shown in Fig. 2 of Ref. 1 seems to be long ranged[5]; the probability for the migrating atom to be trapped at the same location will be small if the range of the potential trap is short. The additional binding energy ΔE_t given in Ref. 1 is the binding energy difference between the trap center and a point $\langle(\Delta r)^2\rangle^{1/2}$ away from the center, which is ~4 Å. When a potential gradient exists on a plane, the walks are no longer random. The mean displacement $\langle\Delta r\rangle$ no longer vanishes. The potential energy gradient in one-dimensional cases can be obtained[6] with the equation

$$\langle\Delta x\rangle=2l\tau(kT/h)e^{-E_d/kT}\sinh(\beta l/2kT), \tag{4}$$

where l is the jumping distance and β is the potential-energy gradient. Unfortunately, the plane size available on field-ion emitter surfaces is in general too small to perform accurate determinations of field gradients.

BINDING ENERGIES

Indeed there are two classes of experiments which can be performed to obtain information on interatomic potentials on surfaces, namely, equilibrium ones and kinetic ones. Let us give an example of the equilibrium experiments. As shown in Fig. 3 of Ref. 1, tungsten adatoms in neighboring channels of W $\{112\}$ planes tend to combine into chainlike clusters. When the chain migrates, the atoms change their bond lengths occasionally from 4.47 to 5.24 Å. Our data show that, at 300 K, the relative frequency for observing the 4.47-Å bonds and the 5.24-Å bonds is $\sim\frac{29}{9}$. Thus the binding energy difference is given by

$$\tfrac{29}{9} = \exp\{[E(4.47\ \text{Å}) - E(5.24\ \text{Å})]/kT\} \qquad (5)$$

or $E(4.47\ \text{Å}) - E(5.24\ \text{Å}) = 30\ \text{meV}$.

In general, equilibrium experiments are difficult to perform in field-ion microscopes to obtain quantitative data on cluster binding energies. Adatoms usually interact strongly enough to combine into a single large cluster within the temperature limit where the substrate plane is stable. Thus one has to rely on kinetic experiments. As pointed out by Johnson and White, the average lifetime before dissociation for a diatomic cluster is related to $E_d + E$. From Fig. 2 one can see that the dissociation is achieved by a sequential activation of an atom over many barriers. Detailed analysis is not available. If one approximates the binding potential with a δ function or the activation to be achieved by one giant step, then the lifetime is given by

$$t \approx (h/kT)\, e^{(E_d + E)/kT} . \qquad (6)$$

For multiatomic clusters, preliminary experiments show that they dissociate by losing one atom at a time. Thus Eq. (6) is equally valid except now E represents the binding energy of an atom in the cluster. Using Eq. (6), the binding energy for a W atom in W clusters on W {110} planes as discussed in Ref. 1 is found to range from 0.26 eV in W_2 to 0.56 eV in W_6. The binding energies are surprisingly low, in disagreement with any bulk theory of crystal binding. W clusters on W {110} have fairly complicated structures. Trying to obtain the interatomic potential over a wide range of distance is difficult. Iridium atoms on W {110} have been found by Bassett[7] to form a closely packed linear chain. Using Eq. (6) and the data given by him, the binding energies are found to be 0.17, 0.35, 0.49, and 0.56 eV, respectively, for an Ir atom in Ir_2, Ir_3, Ir_4, and Ir_5 clusters. The interatomic potential between two Ir atoms on a W {110} plane can be obtained from the data over a wide range of distances by an additional assumption that the interatomic potential energy is additive. Fig. 3 shows the result. It is seen that the interatomic potential is of very long range but exceedingly weak. Although this conclusion is valid only within the specific assumptions made, it is nevertheless quite reasonable for surface atoms. They are much more relaxed and probably have their wave functions extending over a wider distance than the bulk atoms.

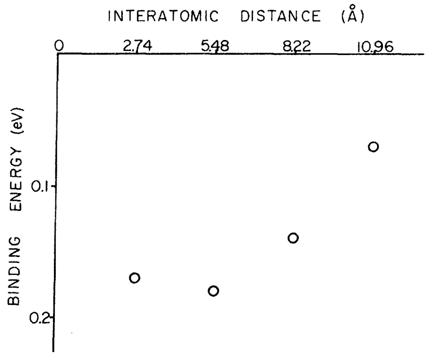

FIG. 3. Interatomic potential energy of two Ir atoms on a W {110} plane.

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