PHYSICAL REVIEW B VOLUME 52, NUMBER 16 15 OCTOBER 1995-II

Scanning tunneling microscopy: Energetics from statistical analysis

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(Received 23 January 1995)

The attraction between two Fe atoms adsorbed on Fe(100) should be much too weak to produce the 0.5–0.7-eV bond that has been deduced by analyzing scanning tunneling micrographs. The assumption that adatom diffusion proceeds by the same mechanism at high and low temperatures may be the source of the discrepancy.

The scanning tunneling microscope (STM) is not just a tool for visualizing the atomic arrangements of surfaces. Beginning five years ago,[1] and culminating in a flood of papers,[2–5] statistical analysis of STM micrographs has been used to provide values of the basic energies that govern how crystals grow. These include the energy required to activate the diffusion of an adsorbed atom or a cluster, and the energy required to split an atom off an adsorbed cluster or a step.

Extracting energetic information from atomic-resolution snapshots has a long history in surface science. For more than two decades, field ion microscopists have been deriving diffusion barriers from the statistics of adatom and cluster displacements, and adatom interaction potentials from adsorbed-dimer pair-distribution functions.[6]

The STM has many advantages relative to the field ion microscope (FIM): It can be used over a much wider range of solids and adsorbed species. It permits one to look at quasimacroscopic single-crystal planes. It also allows one to observe the behavior of steps and other defect structures, and of adsorbed species near them.

On the other hand, with the FIM one looks at the behavior of very few adsorbed atoms, from one up to perhaps six or seven. One also knows when a new atom appears on or disappears from the plane under observation. In STM studies of crystal growth, unseen atoms deposited on the surface, or evaporating off steps, can diffuse without being seen, causing islands to grow or decay from one snapshot to the next. They can also move into or out of the region of observation. Thus, extracting energies from STM studies often involves extensive modeling. Using rate equations,[7] or Monte Carlo methods,[4] one attempts to simulate the statistics of the observations. Energies emerge from the best fit to the data—but they are only meaningful to the extent that the underlying model is well chosen.

Deriving energetics from FIM data is generally simple, though the statistical error in most cases is relatively large because of the small sample size. The opposite is true in STM analyses. There the sample size is typically large, but the physics under observation is much more complex. As a result, the interpretations of energies that emerge from present-day simulations of STM data must be viewed with a healthy dose of skepticism. Only rather simplified growth models are computationally tractable, and the effects of the simplifying assumptions may not be controlled sufficiently well.

These remarks are occasioned by recent STM-based papers[3–5] reporting values of the energy required to separate two Fe atoms initially adsorbed on the Fe(100) surface in adjacent sites. The reported separation energies, between 0.5 and 0.7 eV, are *much* too large to be believed, according to the following reasoning: (1) Two independent FIM measurements imply that the energy to separate an adsorbed W dimer on W(110) is close to 0.3 eV.[8] (2) The cohesive energy of bulk bcc W is 8.7 eV/atom vs 4.3 eV/atom for Fe. Thus cohesion for Fe is only half as strong as for W. (3) Whereas on the quasi-close-packed bcc(110) surface adsorbed atoms can be nearest neighbors to one another, *on a bcc(100) surface, adatoms in adjacent hollows are second neighbors* (see Fig. 1), lying 15% farther apart than the nearest-neighbor spacing. [This amounts to an extra 0.39 Å on Fe(100).] Thus unless the adatoms pay the energetic price of moving away from the fourfold symmetry sites that they occupy as monomers, their direct interaction is considerably weaker than between nearest neighbors. These three facts imply that the energy required to separate adjacent Fe adatoms on Fe(100) should be considerably smaller than 0.15 eV, and certainly nowhere near 0.5–0.7 eV.

Parenthetically, (4) magnetic interactions are much too small to make up the difference—the exchange constant for bulk Fe is on the order of 10 meV. Also (5), Kellogg's

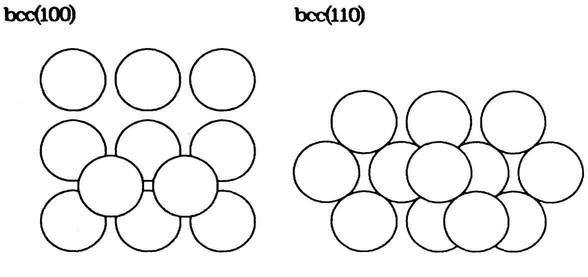

FIG. 1. Schematic top views of a pair of atoms adsorbed in adjacent sites above bcc(100) and bcc(110) surfaces. Atoms are represented by circles whose diameters all equal the nearest-neighbor distance for the crystal. Note that on the (100) surface, the adsorbed atoms are not nearest neighbors. On the (110) surface they are.

FIM study of Ni atoms on W(100) shows that adsorbed Ni dimers dissociate in the same temperature range, 350–400 K, as where Ni *monomers* begin to diffuse.[9] This is an experimental example of a small dimer separation energy in adsorption on a bcc(100) surface.

Stroscio and Pierce[3] (SP) extract the Fe-Fe separation energy from the temperature dependences of the Fe island density and of the island size distribution, as seen in their STM snapshots. According to a standard rate-equation analysis,[7] the slope of a ln(island density) vs inverse temperature "Arrhenius plot" is $(iE_d+E_i)/(i+2)$, where E_d is an activation energy for diffusion, and E_i is the energy to dissociate a "critical island" comprised of i adatoms into i isolated adatoms. In a given temperature range, a cluster of $i+1$ adsorbed atoms is defined to be the smallest island that is immobile and will grow. A "critical" island contains one fewer adsorbed atom. By definition $E_{i=1}=0$, since a one-atom island has no adatom-adatom bond to be broken.

From the island size distribution below 250 °C, SP determine that at low temperatures the critical island size corresponds to $i=1$. Thus at these temperatures an Fe dimer is a growth nucleus, and from the Arrhenius plot they extract the rather small[10] monomer diffusion barrier energy 0.45 ± 0.04 eV. Above 250 °C, the distribution of island sizes changes. By comparison to simulations of Bartelt and Evans,[11] while taking account of the measured island density, SP conclude that the high-temperature critical island size is three Fe adatoms.

Thus from the higher-temperature Arrhenius plot of island density they determine a slope equal to $0.2(3E_d+E_3)$. To extract the value of E_3 from this slope, SP assume that E_d is just what they determined for monomers at lower temperatures. With this assumption, E_3 turns out to equal 1.1 ± 1.0 eV. Since there are two interadatom bonds in a three-atom island, SP conclude that the Fe-Fe bond energy is roughly 0.5 eV, with the rather large quoted error bar.

The fact that this bond energy appears to be much too large demands an explanation. The simplest is that the experimental error bar on E_3 is so large that one need not worry. However, Amar and Family's Monte Carlo analysis of the crossover from small to larger critical island size yields an even larger dimer bond energy, namely, 0.6 ± 0.1 eV.[4] A similar value, 0.7 eV, is obtained in the simulations of Bartelt and co-workers.[5]

Thus, let us question the assumption that E_d is the same in the high- and low-temperature regimes. Suppose that there is more than one mechanism by which Fe adatoms can diffuse, a particularly low barrier process such as concerted substitution,[10] and a second process, such as hopping over a bridge, with a higher barrier but also a higher prefactor. At low temperatures only the low barrier process will occur. But at high temperatures the more energetic diffusion mechanism will also be important and, depending on the prefactors, may even dominate. In this case, using the small diffusion barrier to extract a value of E_3 from the slope of the high-temperature Arrhenius plot, $0.2(3E_d+E_3)$, is a mistake leading to too high a bond energy. If for Fe adatoms on Fe(100) a higher-energy mechanism dominated at high temperatures, and had a barrier of 0.8 eV, for example, then E_3 would be of the order of only 50 meV and the separation energy for an Fe dimer would be a satisfyingly small 25 meV or so.

This discussion is intended as a caution in *all* cases where growth energetics are extracted from the temperature variation of scanning tunneling micrographs. Although measurements of surface diffusion barriers and interadatom binding energies have the potential to revolutionize our understanding of the growth of crystals and of "advanced materials," we are not yet at the point where it is routine to interpret the energies one derives by simulating STM images.

I thank E. H. Chason, G. L. Kellogg, and B. S. Swartzentruber for helpful conversations. Work at Sandia National Laboratories was supported by the U.S. Department of Energy under Contract No. DE-AC04-94AL85000.

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