Surface Roughening Studies by Field Emission

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SURFACE ROUGHENING STUDIES BY FIELD EMISSION

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Abstract

Measurements of surface self-diffusion by the field emission fluctuation method along the zones (011)–(112) and (011)–(001) of a tungsten emitter show both 2 and 1 dimensional diffusion, attributed to diffusion of W atoms on the terraces and of kinks along the edges of the stepped surfaces found in these zones. At 950 K – 1000 K the steps along (011)–(112) disorder completely, as indicated by the merging of the two types of diffusion into a single, 2-dimensional regime. Along (011)–(001) definite transitions can only be seen on (023) and (017). The transition temperatures are much lower, ~ 750 K.

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Introduction

Roughening of stepped crystal surfaces is a subject of considerable recent interest. To date the problem has been mainly attacked by structural methods.[1,2] Clear evidence for roughening also comes from the surface self-diffusion behavior of substrate atoms and other defects on stepped surfaces, as will be shown. We use here the field emission fluctuation correlation method,[3,5] in which the emission current fluctuations from a region of ~ 100 Å radius, or more specifically their time autocorrelation function is determined. If current fluctuations are caused by diffusion of ad-atoms or other defects, the current correlation function $f_i(t)$ has a simple theoretical form.

$$f_i(t) \propto \frac{<(\delta n)^2>}{A} \int_A d^\alpha x \int_A d^\alpha x' \frac{e^{-|x-x'|^2/4Dt}}{(4\pi Dt)^{\alpha/2}} \tag{1}$$

$<(\delta n)^2>$ is the mean square fluctuation of the number of diffusing species in the probed region of area A, D the diffusion coefficient, and α the dimensionality of the diffusion process. It follows from Eq. 1 that for 2-dimensional diffusion the correlation function is proportional to t^{-1} at long times, while for 1-dimensional diffusion the function becomes proportional to $t^{-1/2}$, t being time. In the present case, where diffusing entities can be both created and destroyed, it is also necessary to consider the effect of these processes on diffusion. It turns out that the form of the correlation function is preserved, but that the diffusion coefficient D is modified to take into account that the diffusing entity, say an atom on a terrace, may spend a fraction of its time adsorbed at a step edge:

$$D \to D\tau_A / (\tau_A + \tau_B) = D/(1+K^{-1}) \tag{2}$$

where τ_A and τ_B are, respectively, the mean lifetimes in the mobile and (edge) adsorbed states and $K = \tau_A/\tau_B$ is the equilibrium constant between adsorbed and mobile atoms.

The Zone (011)–(112)

A prime candidate for observations is the zone (011)–(112), consisting of terraces and steps of <011> orientation; the steps are close-packed atom rows running along <111> directions. When correlation functions are measured in this zone with a round probe area of ~ 100 Å radius, the number of steps in

the probe region is typically 10–20 and the terrace widths are 8 to 5 Å, depending on orientation of the probe region. These were (257), (123) and (357). In each of these locations 2-dimensional diffusion was found. For T = 450 − 600 K, E = 8 Kcal/mole and $D_0 = 10^{-8} cm^2 sec^{-1}$. As T increases both E and D_0 change, becoming 16–17 Kcal/mole and $10^{-5} cm^2 sec^{-1}$. The reason for this increase is not clear; it may have to do with polaronic effects. The fact that 2-dimensional diffusion is observed is itself remarkable, indicating that diffusing atoms can "climb" steps. In addition to this relatively fast diffusion a second type was observed for T ⩾ 750 K by using much longer correlation times. (For these times the fast diffusion correlation function washes out to zero). This diffusion turned out to be one-dimensional, suggesting that it occurs along the step edges. Its activation energy was found to be ∼ 13 Kcal/mole and the prefactor $D_0 \sim 10^{-11} cm^2 sec^{-1}$. The mean square fluctuations, which are proportional to the concentration and compressibility of diffusing entities[3] show markedly different temperature behavior for the two types of diffusion. Over the range indicated both increase exponentially with 1/T, suggesting that the corresponding energies, 7 Kcal/mole for 2-dimensional and 19 Kcal/mole for one-dimensional diffusion are the heats of formation of the diffusing entities. The differences in these energies and the vast differences in prefactor D_0 suggest that 1-dimensional diffusion along the steps corresponds to that of kinks (and probably kink-antikink combinations) while 2-dimensional diffusion probably corresponds to that of W atoms on the terraces.

As T is increased both diffusion coefficients at first increase in the expected manner, $D = D_0 \exp-(E/kT)$. (Fig. 1) At ∼ 875 K (the exact temperature depending only slightly on orientation) the 1-dimensional diffusion coefficient quite suddenly decreases until T = 925 K. At this point it increases again but now corresponds to 2-dimensional diffusion. The explanation seems quite clear: as T increases above 875 K the steps disorder sufficiently to impede 1-dimensional diffusion along them. Between 925 and 950 K this disorder becomes so great that steps are no longer well defined and diffusion along them is no longer a meaningful concept − diffusion has become 2-dimensional. What about the initially faster 2-dimensional diffusion, i.e., diffusion on and across the terraces? For this process D continues to increase until T = 900 K and then decreases sharply. Above 1000 K only a single 2-dimensional diffusion regime can be seen. This behavior is just what one would expect. Above 1000 K the terraces have essentially disappeared because of the step disordering. We can thus assign the roughening transitions a temperature of 1000 K, although sufficient step disordering to destroy 1-dimensional diffusion occurs already at 950 K. Surprisingly these temperatures do not vary much with terrace width, possibly because of the very limited range available.

The Zone (011) – (001)

What about stepped surfaces of other orientation? An obvious candidate is the zone (011) – (001). Along this zone the terraces are (011) planes, the steps are (001) segments and edges run along the <001> direction and thus are not close-packed. Similar experiments on (023) (Fig. 2) again reveal two diffusion coefficients which merge into a single one at much lower temperature, 675 K. This time both coefficients are 1-dimensional below the transition. This suggests that W atoms cannot now climb the steps. The activation energy and D_0 for fast diffusion for

450 ⩽ T ⩽ 650 K are essentially the same as on the zone (011) – (112), suggesting that the same diffusion process occurs on the (011) terraces in both cases and also that climbing (111) oriented steps does not seem to decrease D very much. The slower diffusion has lower activation energy, 9.9 Kcal/mole and a higher prefactor, $D_0 = 4 \times 10^{-9} cm^2 sec^{-1}$ than along the (011) –(112) zone, suggesting that kinks move more easily along the <100> direction. The formation energies of ad-atoms and kinks, respectively, are also much smaller than for close packed step edges: 3.5 Kcal/mole for atoms and 8 Kcal/mole for kinks. The ratios of these energies, interestingly enough are nearly the same, however, for the two cases.

Further along the (011) – (001) zone, i.e., (012) and (013) two diffusion regimes are difficult to see. (Fig. 3) As (001) is approached, namely for (017) orientation two regimes again emerge clearly; again they are both 1-dimensional and show a transition at ∼ 770 K. The diffusion activation energies and prefactors are 6.7 Kcal/mole and $9 \times 10^{-9} cm^2 sec^{-1}$ and 10 Kcal/mole $3 \times 10^{-9} cm^2 sec^{-1}$, respectively; that is, both differ from anything seen along the (011) –(112) zone or on (023). This suggests that steps and terraces have become reversed. In the intermediate regions, i.e., (012) and especially (013) there are only hints of a transition, since the surface can only formally be described in terms of steps and terraces.

Conclusion

The preceding has indicated rather clearly that roughening on well defined stepped surfaces can be observed in the manner outlined and that step roughening precedes global roughening. It could be asked to what extent the electric field, ∼ 3 × 10^7 volts/cm, present during the experiments affects the results. It is entirely possible that the field can cause changes of 1–2 Kcal/mole in the activation energy of diffusion of single atoms,[4] but is likely to affect kinks less. It may also have some effect on roughening but it is not clear whether it would lower the roughening temperature significantly. It would be interesting to compare measurements on Ni by the present method with those of Engel[1,2] by a diffraction method. Apart from this a number of interesting questions are raised but not answered by this work. Why is step climbing apparently easy for (111) oriented but not for (001) oriented steps? What are the diffusing kinks? Are they single atom (negative) kinks or larger entities? The relative energies for atom and kink formation as measured here suggest mostly single atom (negative) kinks. Why are their formation energies in the zone (011) – (001) so low? Evidently it would be interesting to extend this work to other substrates.

References

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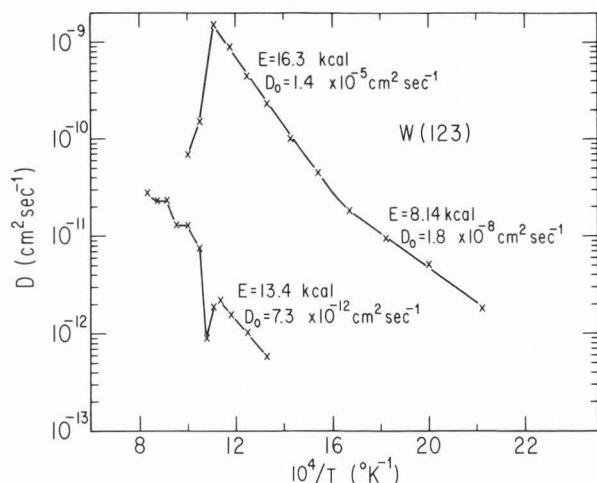2. Conrad EH, Aten RA, Kaufman DS, Allen LR, Engel T,

Fig. 1. Semilogarithmic plots of diffusion coefficients D vs. 1/T on W(123). Activation energies E and prefactors D_0 are indicated for each regime on the figure. The upper curve corresponds to 2-dimensional diffusion at all T. The lower curve corresponds initially to 1-dimensional diffusion as discussed in the text.
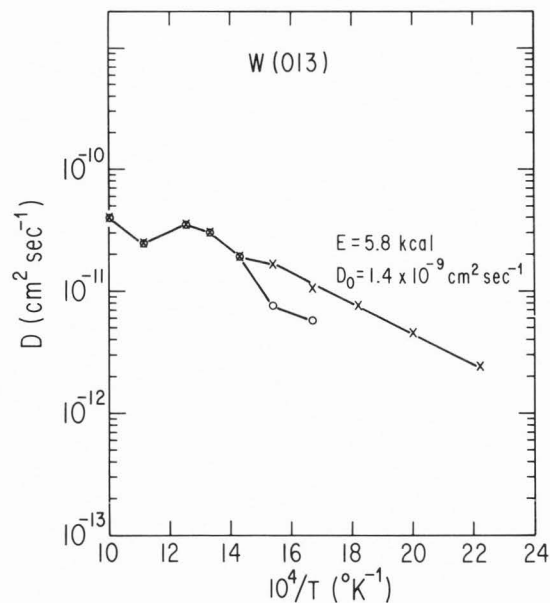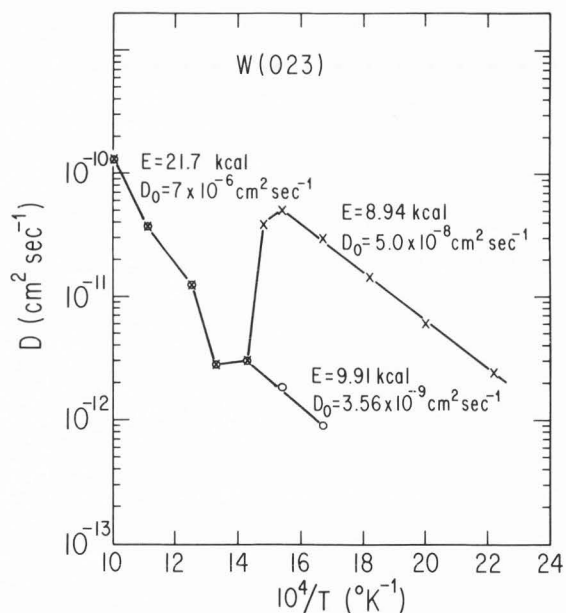

Fig. 2. Log D vs. 1/T on W(023). Activation energies E and prefactors D_0 for each regime are indicated on the figure. All observed diffusion regimes are 1-dimensional.

Fig. 3. Log D vs. 1/T on W(013). Activation energy E and D_0 where measurable are indicated on the figure. All diffusion was 1-dimensional.

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Discussion With Reviewers

R.W. Vook: Could a high potential along with temperature act as driving forces for the formation of "whiskers" under any reasonable set of circumstances that involve either monocrystalline or polycrystalline materials?

Authors: Field induced build-up occurs but at considerably higher temperatures on tungsten. The resultant emitter shape does not involve whiskers however, but simply slight protrusions.

R.W. Vook: Is there any corresponding direct evidence, e.g. by FIM, for the 1 and 2D diffusion discussed in the text?

Authors: To the best of our knowledge only 1- and 2-dimensional single atom diffusion has been looked at. I am not aware of attempts to look at kink diffusion. The 2-dimensional diffusion observed here agrees reasonably well with corresponding single atom observations by the FIM, at least on close-packed terraces.

H. Adachi: It is widely known that heating a sharp needle without applied electric field gives round smooth apex and I believe that this is a result of random diffusion. Now I have a question: Could you detect any effect of the applied electric field on the direction of diffusion?

Authors: No field effect on the direction diffusion was seen, but it is not clear how it would show up.

H. Adachi: What is the difference between the heating conditions for giving a round smooth apex and for the roughening?

Authors: There is no essential difference. On recooling, the emitter resumes its thermally annealed end form. It should be understood that the roughening discussed here applies only to a few atom layers at the emitter surface, not to its gross shape.

M. Gesley: How might polarons account for the two experimental observations that (i) there is a two orders of magnitude increase in two-dimensional diffusivity on the (011) – (112) zone and (b) no corresponding phase change noted by the total noise power measurement? In other words how can a cooperative effect that radically changes the potential well-depth and configurational entropy presented to the diffusing entity not affect its compressibility?

Authors: We are not sure that we understand this question. Small polarons are very local and their participation in tunneling diffusion has no particular relation to phase transitions. There may well be an effect on compressibility, but in the present case the dominant effect, at least initially, seems to be that the density of diffusing entities is not constant, as in diffusion of adsorbed species, like O or H atoms, but depends on temperature. Thus the exponential increase in f(0) with 1/T.

M. Gesley: Are the $<(\delta N)^2>$ data for slow one-dimensional diffusion obtained by an extrapolation back to $t = 0$ of the $t^{-\frac{1}{2}}$ part of the autocorrelation functions?

Authors: No. The initial short time regime is extrapolated to $t = 0$.

M. Gesley: From the noise power data it appears easier to form adatoms than kinks. Can this be justified by a bond-breaking argument, and is this why the ratios of these formation energies are nearly the same for both zones studied?

Authors: There are simple bond breaking arguments, but we are not sure how valid they are. At low temperatures, where steps have no disorder, a detached atom could only be formed by creating first a negative kink and a positive kink, the latter then detaching to give a free atom and leaving behind a negative kink. On this basis the formation of a negative kink-positive kink pair requires the breaking of 3 bonds, while the final state, negative kink plus free atom requires a total of 4 bonds being broken. However, at high temperature where there already are complicated negative and positive kinks, it may be that the formation of a detached atom only requires the breaking of a single bond. If so, the ratio of roughly 3 : 1 for kink to free atom formation might be explained and this could carry over to the non-close-packed steps.

M. Gesley: What happens to the form of the autocorrelation function and particularly the crossover between t^{-1} and $t^{-\frac{1}{2}}$ behavior as the roughening transition is approached?

Authors: We have not looked at this in detail. AT 925 K diffusion is still essentially 1-dimensional, at 950 K it is already 2-dimensional.

M. Gesley: Given the applied electric field distorts the potential trough presented to diffusing entities, why would this not affect kinks as well as adatoms?

Authors: The field undoubtedly affects kinks also, but there is no real way of estimating the magnitude of the effect.