Disordering kinetics in surface overlayers

A. Jesina and M. C. Tringides

Ames Laboratory, Department of Physics, Iowa State University, Ames, Iowa 50011-3020

(Received 27 October 1992; revised manuscript received 11 February 1993)

The disordering kinetics of the O/W(110)-$p(2\times1)+p(2\times2)$ overlayer, prepared initially in a well-ordered state, are studied with low-energy electron diffraction profile analysis. The decay of the peak intensity, used as a measure of the growing disorder, cannot be fitted to a power law as in the case of ordering processes. The full width at half maximum of the time-dependent structure factor $S(q,t)$ is constant with time, which suggests that the average size remains constant. Diffusion activation energy extracted for the temperature dependence of the disordering is 1.0 ± 0.05 eV, which is different from the value of 0.6 eV measured in ordering processes. The difference can be explained by the adsorbate-adsorbate interactions, which contribute differently to the diffusion barrier, in the two experiments.

The evolution of a surface overlayer towards equilibrium, after a quench from an initial to a final state of different symmetry, has revealed[1] the growth laws that control nonequilibrium processes. The most common thermodynamic parameter used in the quench is the temperature T, and all the experiments performed so far on two-dimensional systems monitor the evolution of a system from an initial random to a final ordered state. The change of symmetry and the time dependence of the growing domains can be easily monitored with diffraction.[2] In such ordering experiments it has been verified that the average domain size L grows like a power law in time $L = A(T)t^x$, with $A(T)$ a temperature-dependent growth rate and x a universal exponent which is independent of the details of the system. In addition, the domain size distribution is time invariant, suggesting self-similar growth, as measured from the scaling of the nonequilibrium structure factor $S(q,t)/S(0,t)=F[q/w(t)]$, where $w(t)$ is the full width at half maximum (FWHM) at time t. Additionally these experiments, if repeated at several final temperatures, can determine[3] the temperature-dependent growth rate $A(T)$ and by using a simple dimensional argument, one can establish that the diffusion coefficient is related to $A(T)$ with the relation $D\alpha A^{1/x}$. This implies that the diffusion activation energy can be extracted from the growth rate activation energy $E_D = E_A/x$.

Several ordering experiments[3–5] have verified the above predictions. In particular,[3(b)] for the O/W(110)-$p(2\times1)+p(2\times2)$ system, a growth exponent of $x = \frac{1}{3}$ was measured extending the validity of the Lifshitz-Slyozov growth law to systems with finite-density, multidegenerate, separating phases. The diffusion activation energy extracted from this ordering experiment is $E_D=0.6\pm0.05$ eV. This is considerably lower than the diffusion activation energy $E_D=1\pm0.05$ eV measured[6] in an equilibrium experiment with the current fluctuation method. In the fluctuation method, the overlayer is equilibrated with the (2×1) and (2×2) phases fully developed, while in the ordering experiment, the average overlayer configuration is, at least initially, random. The difference between the activation energies in the two experiments was attributed to the adsorbate-adsorbate interactions that are present in O/W(110). A lattice-gas model with competing interactions (nearest-neighbor attractive and next-nearest repulsive interactions) is a good description[3(a)] of the system. The interactions contribute differently to the diffusion barrier in the two experiments, because the overlayer configuration is different. In the equilibrium experiment the attractive interactions have a larger contribution and can account for the observed 0.4 eV difference with the ordering experiment.

Although a considerable amount of work[7] has been performed to measure surface diffusion, most of the available techniques are limited to noninteractive systems. In most of the techniques in current use, the solution of the linear diffusion equation in a given geometry is compared to the measured profile. For systems with interactions, however, the diffusion coefficient becomes coverage dependent and the nonlinear diffusion equation should be employed. Solutions to nonlinear diffusion equations are nontrivial, so it is not clear to which theoretical expression the measured quantity should be compared. Ordering experiments, however, provide a method to measure surface diffusion coefficients on interactive systems, because an easily measurable signal can be fitted to a simple expression (the power law) to extract $A(T)$, and the diffusion coefficient.

Systems under strongly nonequilibrium conditions are also realized during the opposite process of disordering. Initially the system is in a well-equilibrated state and the domains formed have a maximum size. The system is raised to a higher temperature where the disordered state is present. We ask similar questions as posed above, such as what are the growth laws controlling the evolution of disorder, is there universality, how can a diffusion barrier be extracted from the temperature dependence of the disordering process, and how does it compare to the one measured in an ordering process. Despite the recent emphasis[1] on studying ordering processes both theoretically and experimentally, no systematic study of disordering processes was undertaken to address the above questions.

The experiments were carried out on the O/W(110)-$p(2\times1)+p(2\times2)$ system at high coverage. It is the prototype of a surface overlayer to test coll⌐'tive two-dimensional (2D) phenomena, both at equilibrium and at nonequilibrium. We concentrate on the high coverage $\theta=0.68$, to test the role of the overlayer configuration in determining the diffusion barrier, by comparing the disordering to the ordering experiment. If the system is heated up to $T=550$ K, a $(2\times1)+(2\times2)$ diffraction pattern is formed, as evidenced by the fully developed $(\frac{1}{2},0)$ and $(\frac{1}{2},\frac{1}{2})$ spots. After heating in the range 600–800 K the $(\frac{1}{2},\frac{1}{2})$ spot decreases in intensity over a period of several minutes, well within the time resolution of the acquisition system. Above 800 K the loss of the superstructure intensity is too fast to be followed by the detector. Similar changes within the high coverage overlayer have been previously observed in an earlier study[8] of the equilibrium structure of the system.

Experiments were carried out in a UHV system[3(b)] of base pressure 8×10^{-11} Torr, equipped with a low-energy electron diffraction (LEED) diffractometer, cylindrical mirror analyzer, and a mass spectrometer. Diffraction images were recorded with a silicon-intensifier-target video camera, digitized with a commercially available imaging board, averaged for improving the S/N ratio, and stored on an IBM-AT computed for further analysis, to extract quantitative information about the evolving domains. A low thermal mass sample holder was built, to respond quickly to the temperature quench. The sample temperature can vary from 130 K, where oxygen is initially deposited up to 2200 K for sample cleaning with electron bombardment.

Figure 1 shows typical results at $T=664$ K of the time-dependent angular profiles $S(q,t)$ of the $(\frac{1}{2},\frac{1}{2})$ spot, as the system is quenched from the initial state at $T=550$ K. Similar results are observed at all final temperatures.

During the disordering process the FWHM's stay constant, well below the expected increase, for the corresponding decrease in peak intensity. This is opposite of what was previously observed in ordering processes, where ordering profiles show self-similarity with a time-dependent FWHM. Similar constant FWHM's during disordering processes have been observed in other systems.[9] Instrumental limitations are possibly more pronounced in disordering processes because the initial domain sizes are larger. However, the initial $(\frac{1}{2},\frac{1}{2})$ FWHM was $2\frac{1}{2}$ times broader than the instrument response function, possibly because of the eight different types of domains that are present at $t=0$. We have estimated the effect of the instrument by convoluting a Gaussian instrumental function with a Lorentzian line shape (which is $2\frac{1}{2}$ times broader than the Gaussian FWHM) to be less than 10% for the peak intensity and 3% for the FWHM.

Surprisingly, during the disordering of the $(\frac{1}{2},\frac{1}{2})$ spot, a linear relation exists between the peak and the full 2D integrated intensity over the $(\frac{1}{2},\frac{1}{2})$ Brillouin zone (BZ). The integrated intensity is changing, because most probably monomers released out of the ordered domains redistribute diffracted intensity outside the $(\frac{1}{2},\frac{1}{2})$ BZ. We have used the decay of the integrated intensity as a measure of the growth of the disordered phase, since the constant FWHM is not appropriate. Figure 2 shows the integrated intensity vs time at several final temperatures. It is clear that the decay is faster at the higher temperature. The functional form of the decay is not exponential, and the long-time behavior has extremely slow varying tails. The initial fast decay of the intensity is followed by a slow varying regime. The intensity at the leveling off is higher, for lower annealing temperatures.
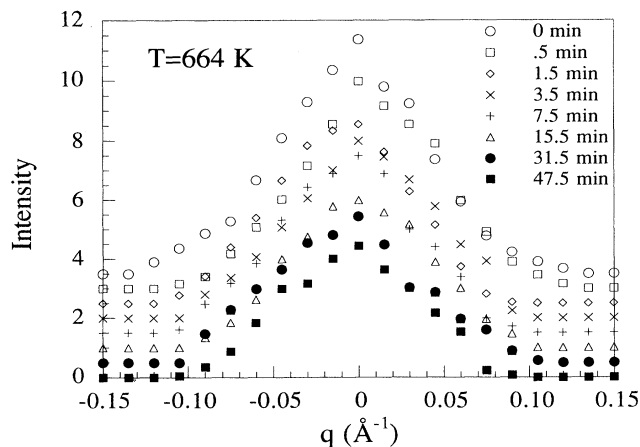
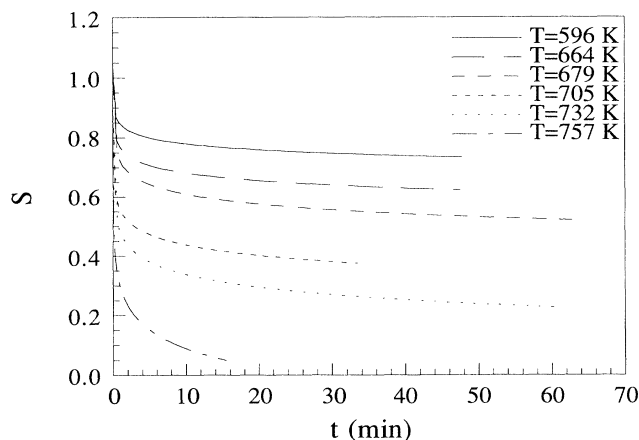The wide range of temperatures used allows us to con-

FIG. 1. Plot of the angular $(\frac{1}{2},\frac{1}{2})$ profiles obtained successively at different times with the substrate temperature $T=664$ K. The FWHM's are constant.

FIG. 2. The decay of the $(\frac{1}{2},\frac{1}{2})$ normalized 2D integrated intensity vs time at different substrate temperatures. All the curves have initially a unity value but they have been shifted by a constant amount for clarity. No power law can be fitted to the growing among of disorder measured by $[I(0)-I(t)]$. The intensity approaches a temperature-dependent saturation value at long times.

centrate either on the late time slow regime (at low temperatures) or on the early fast decaying regime (at high temperatures). We search for a power-law time dependence of the growth of disorder by plotting $[I(0)-I(t)]/I(0)$ vs t, to test if power laws that are characteristic of ordering processes also describe disordering processes. The leveling of the intensity is not consistent with power-law decay. Because the domains are smaller than the coherence length by more than a factor of $2\frac{1}{2}$, instrumental effects, as mentioned before, are less than 10%. A power-law ft, at the higher temperatures, where the leveling off is unimportant, to extract an effective growth exponent is not of high quality and it gives a low value $x=0.3$. This is equivalent to a growth exponent of $x=0.15$ for the average domain size of the disordered phase (under the usual assumption that the average domain size is proportional to the square root of the peak intensity), well below the $x=\frac{1}{3}$ value obtained for ordering processes. Power-law decay is not observed in other disordering studies.[9,10]

As a test of the observations described above, we have performed Monte Carlo simulations on a model system to check the absence of a power-law decay during disordering. A Hamiltonian, with (2×1) and (2×2) ground states was not used, because it is more difficult to handle computationally, and extensive runs would be needed to obtain good statistics. We chose, instead, a simpler system, the Ising model with nearest-neighbor repulsion that has the $c(2\times2)$ phase, as the ground state. The ordering growth kinetics of the model have been studied[1] extensively, both analytically and with simulations, and the growth exponent is $x=\frac{1}{2}$. If disordering obeys a similar law, we would expect a linear decay of the intensity in Fig. 3. The system is initially prepared in a perfect $c(2\times2)$ phase and the loss of order is monitored from the decay of the Bragg peak intensity evaluated at $(\pi/a, \pi/a)$, the Bragg condition for the $c(2\times2)$ domains. The system initially in a perfectly ordered $c(2\times2)$ phase is
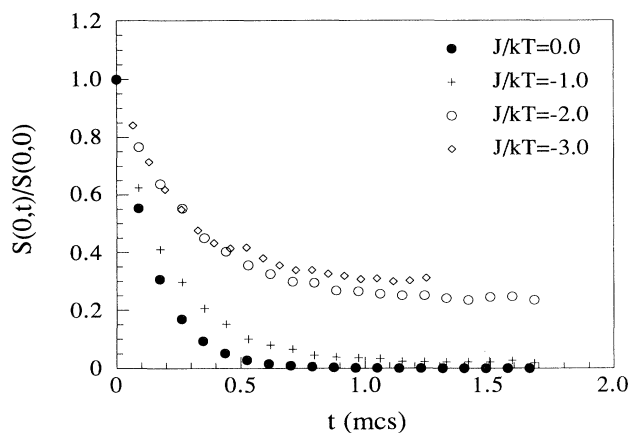

FIG. 3. Monte Carlo simulation results obtained for the decay of the peak intensity. The system is initially in a perfect $c(2\times2)$ state, chosen because of the computational efficiency. No power law can befitted to the growth of disorder $[I(0)-I(t)]$ and long-time saturation is observed as in the experiment.

upquenched at several temperatures $-3<J/kT<0$ which includes states in both the ordered and disordered regions. The critical point for this model at coverage $\theta=0.5$, the ideal coverage of the $c(2\times2)$, is at $J/kT=-1.86$. Spin exchange, i.e., diffusive dynamics, were followed. The details of the simulation can be found elsewhere.[11] The results are shown in Fig. 3 and it is clear that the time dependence is not linear with time, thus verifying the absence of a power-law with $x=\frac{1}{2}$. Long-time leveling off tails are observed in the simulations, reminiscent of the experimental observations in Fig. 2. It is clear that if the disordering kinetics of this well-studied case of the $c(2\times2)$ phase, prepared in a single domain initially, is not similar to the kinetics for ordering processes, then for more complicated ordered structures that have multidegenerate phases [i.e., $p(2\times1)+p(2\times2)$] and more complicated domain size distribution, stronger deviations from power-law time dependence should be expected.

A previous Monte Carlo study[12] of the ordering kinetics of the same model has monitored with time how a circular region, prepared in one of the two equivalent $c(2\times2)$ phases and surrounded by the other phase is eliminated with time. The competition between the two equivalent phases, driven by the excess free energy in the boundary, leads to a linear time dependence of the decreasing domain size and therefore a growth exponent $x=\frac{1}{2}$. This shows clearly that the growth of the disordered phase is distinct from the elimination of an ordered phase, surrounded by the equivalent ordered phase of different type. The latter case is a case of curvature driven growth, between adjacent degenerate phases, while the absence of degeneracy in the growth of the disordered phase is most likely the reason for the asymmetry observed in the growth laws.

We have discussed previously that nonequilibrium experiments, performed at different temperatures, provide information about surface diffusion which is the mechanism by which equilibrium is restored in the system. Although no analytic results exist of how the surface diffusion coefficient D is related to the decay of the peak intensity, we can assume that it is proportional to the initial slope. Such an analysis of using the initial slope of the diffracted intensity to extract the diffusion coefficient has been used previously in a LEED study.[13] It is clear from Fig. 2 that as the temperature is increased the intensity decays at a faster rate. We can assume that the decaying intensity is a function of the combination (Dt) which dimensionally has units of length. An expansion at $t=0$ for short enough time produces $I(t)=I_0(1-cDt+O(Dt)^2+\cdots)$ showing that indeed the initial slope is proportional to the diffusion coefficient. The only exact result[14] for the disordering of an initially $c(2\times2)$ 1D ordered state is in agreement with the expansion. Figure 4 plots the initial slope vs $1/T$ to test for Arrhenius temperature dependence. A list square fit gives $E=1.0\pm0.005$ eV. This differs by 0.4 eV from the value found in the ordering experiment and is similar to the value measured in equilibrium experiments. Is this expected? We have discussed previously the contribution of adsorbate-adsorbate interactions to the diffusion bar-
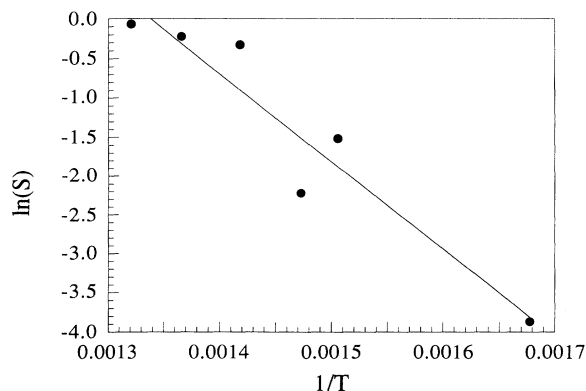
FIG. 4. Plot of the initial slope $\ln S$ vs $1/T$ of the 2D integrated intensity decay, measured from Fig. 2. An activation energy 1.0 ± 0.05 eV is measured which is higher by 0.4 eV from the activation energy measured in the ordering experiment, because of the interaction contribution.
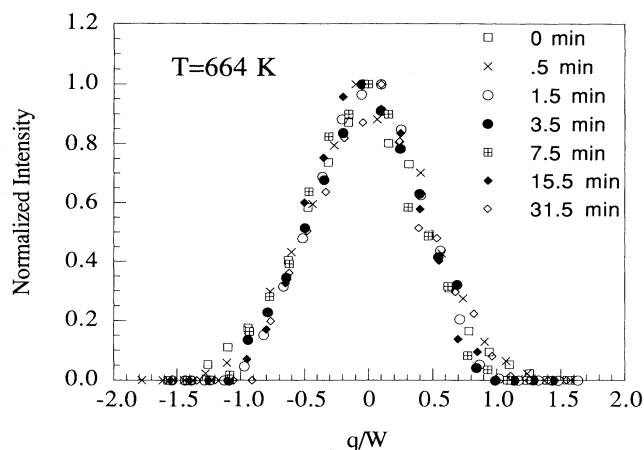

FIG. 5. $S(q,t)/S(0,t)$ vs $q/w(t)$, where $S(q,t)$ is the nonequilibrium structure factor and $w(t)$ the FWHM at time t plotted to test whether scaling is obeyed. Deviations at the "wings" of the profile are related to the constantly increasing monomer number while the number of larger domain sizes is decreasing at a constant rate.

rier, which depends on the configuration of the overlayer. In the disordering experiment the initial arrangement of the atoms is similar to the equilibrium experiment, since the ordered phases are fully developed. Mostly, the attractive nearest-neighbor interaction contributes to the barrier, which raises the activation energy by 0.4 eV. Therefore, ordering and disordering experiments performed in parallel can provide detailed information about surface diffusion, the energetics controlling it, and the role of the interactions.

The almost constant FWHM is a puzzling feature of the disordering processes. It has also been observed in previous studies.[9] It was explained before by the highly anisotropic vacancy mobility within the dimer rows that effectively reduces diffusion to 1D process. In the current experiment, we have a full 2D process because of the rhombic symmetry of the substrate. The constant FWHM suggests that the average domain size distribution is constant. Initially, the surface is covered with large domains of different degeneracy, because each phase is fourfold degenerate. Several different mechanisms are consistent with an invariant average size. Disordering involves first the rate of nucleation of the disordered phase within the ordered domains (which is expected to be larger for larger domains) and the rate of elimination of the whole domain (which is expected to be lower for larger domains). It is possible that the two rates compensate each other, so the probability of eliminating a domain is independent of its size. If this is the case, the fraction of domains eliminated will be the same for all sizes. This mechanism not only maintains the same average size during disordering but it implies that the domain size distribution is time invariant, i.e., scaling holds. Figure 5 shows $S(q,t)/S(0,t)$ vs $q/w(t)$ to test for this invariance, where $S(q,t)$ is the profile at time t and $w(t)$ the FWHM of $S(q,t)$ Although there are deviations from a perfect collapse of the data onto a universal curve, the deviations are not more than 15% and they are more pronounced at the "wings." Deviations at the "wings" reflect the increasing number of smaller size domains, while the number of larger size domains de-

creases as described above at a constant rate. Additional evidence supporting scaling is the linearity observed between peak and 2D integrated intensity, which would have been violated if $S(q,t)$ does not follow the same functional expression at all times. It is interesting to address the question of scaling theoretically, to determine to what extent it is valid during disordering and if there are deviations as observed experimentally.

We have studied the disordering kinetics in a surface overlayer as a function of time at several final temperatures. Contrary to ordering processes, no power-law growth with universal growth exponents is obeyed. A leveling off is observed, which is lower for higher, final quench temperatures. Monte Carlo simulations on a model system confirm this result. The FWHM's are constant during the disordering process, suggesting that the average size is invariant with time. As deduced from the almost time-independent profile line shapes, the probability of eliminating domains is size independent for large domain sizes. The absence of degeneracy in the disordered phase might be responsible for the absence of power law in the decay of the intensity and the constant FWHM's. Activation energy extracted from the decay of the peak intensity is 1.0 ± 0.05 eV, in agreement with the results of equilibrium experiments, confirming the role of the overlayer configuration in modifying the diffusion barrier. Ordering and disordering processes provide very large experimental signals, because of the catastrophic change in the symmetry of the system, to be used as a universal method to determine surface diffusion coefficients in systems with interactions.

[1]Ole G. Mouritsen, in *Kinetics of Ordering and Growth at Surfaces,* edited by M. G. Lagally (Plenum, New York, 1990).

[2]G. G. Wang, J. K. Zuo, and T. M. Lu, in *Phase Transitions in Surface Films 2,* edited by H. Taub, G. Torzo, H. J. Lauter, and S. C. Fain, Jr. (Plenum, New York, 1990), p. 455.

[3](a) P. K. Wu, M. C. Tringides, and M. G. Lagally, Phys. Rev. B **39**, 7595 (1989); (b) M. C. Tringides, Phys. Rev. Lett. **65**, 1372 (1990).

[4]J. K. Zuo, G. C. Wang, and T. M. Lu, Phys. Rev. Lett. **60**, 1053 (1988).

[5]J. K. Zuo and J. F. Wendelken, Phys. Rev. Lett. **66**, 2227 (1991).

[6]M. C. Tringides and R. Gomer, Surf. Sci. **155**, 254 (1985).

[7]R. Gomer, Rep. Prog. Phys. **53**, 917 (1990).

[8]E. Bauer and T. Engel, Surf. Sci. **71**, 695 (1978).

[9]M. C. Tringides, J. H. Luscombe, and M. G. Lagally, Phys. Rev. **39**, 9377 (1989).

[10]R. Spitzel, H. Niehus, B. Poelsema, and G. Comsa, Surf. Sci. **239**, 243 (1990).

[11]M. C. Tringides, Surf. Sci. **250**, 260 (1991).

[12]P. S. Sahni, G. S. Grest, and S. A. Safran, Phys. Rev. Lett. **50**, 60 (1982).

[13]K. Heinz, G. Schmidt, I. Hammer, and K. Müller, Phys. Rev. B **32**, 6214 (1985).

[14]J. W. Evans and D. K. Hoffman, Phys. Rev. B **30**, 2704 (1984).