Dynamics of Two-Dimensional Ordering of an Overlayer with Fourfold-Degenerate Ground State: W(110)p(2×1)-O

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The dynamics of ordering of W(110)p(2×1)-O has been studied at two coverages with use of low-energy electron diffraction. Island coarsening and diffusion-limited island growth mechanisms are identified at the coverage corresponding to two-phase coexistence, while in the one-phase region, domain growth is observed. In all cases, the increase in the average size of ordered regions follows a $t^{1/2}$ dependence. Activation energies and frequency factors are extracted.

The dynamics of ordering of commensurately adsorbed overlayers has recently attracted considerable theoretical interest.[1-8] Much of this interest centers around the differences in domain-growth kinetics for systems that have different ground-state degeneracies. A disordered overlayer quenched to a temperature at which an ordered phase is expected on thermodynamic grounds may order in two possible ways, depending on whether the quench is into regions on the phase diagram in which one phase is stable or two phases can coexist. A quench into a one-phase region produces small domains that cover the whole surface but are separated by domain boundaries. These domains grow with time, driven by domain-wall curvature. Hence small domains disappear. For a quench into a coexistence region, initially small islands nucleate and grow at the expense of the disordered system, until two-phase equilibrium is achieved. The two phases may be the ordered structure and an "empty-lattice" or vacancy phase, or they may be two different ordered structures. The driving force for growth is the net cohesive energy of the ordered islands. Subsequent growth, driven by island boundary curvature, may occur at a later stage, as small islands (or domains if the islands now meet) disappear at the expense of larger ones (called "coarsening" of the ordered phase).

The dynamics of domain growth in an overlayer quenched into a one-phase region has attracted particular attention. The growth of the average domain size is expected to follow a power law of the form $L(t) \propto t^x$, where L is the average diameter, t is the time, and x is some "universal" constant that depends on the degeneracy, p, of the ground states that the overlayer ordered regions can form. The role of multidegenerate ground states in domain-growth kinetics was first suggested by Lifshitz.[9] He argued that domains for two-dimensional systems in which $p > 3$ will evolve quite slowly because of the influence of boundaries in inhibiting the growth. The role of boundary curvature in domain growth has been emphasized.[10] All theories agree that, for $p = 2$, $x = \frac{1}{2}$. This has also recently been shown experimentally[11] for ordering in W(112)p(2×1)-O, at least for short times, before the order parameter exceeded a value of 0.5.

In this Letter, we report low-energy electron-diffraction (LEED) results for the ordering of p(2×1) oxygen islands or domains on W(110), a symmetry for which the nature of the growth law is much more controversial. W(110)p(2×1)-O belongs to the class of *XY* models with cubic anisotropy,[12] with a ground-state degeneracy of $p = 4$, namely the p(2×1) and p(1×2) domains and two translational antiphase domains for each of these. There appears to be at present no agreement theoretically on the value of x for $p = 4$ systems.[3] We present results at two coverages. One is at the saturation coverage for the p(2×1) structure, the coverage corresponding to the measurement reported in Ref. 11 and discussed in most of the theoretical studies. We demonstrate that the growth is proportional to $t^{1/2}$ at all but very short times. The second coverage is lower. The p(2×1) and lattice-gas phases coexist at this coverage at sufficiently low temperatures.[13] We demonstrate that the growth rate at this coverage is different from that at the saturation coverage, but that a $t^{1/2}$ dependence is maintained. We derive activation energies and frequency factors for ordering at both coverages.

Oxygen was adsorbed onto W(110) at 80 K, a temperature at which the oxygen does not form an ordered pattern. The overlayer can therefore be described as an immobile lattice gas. The overlayer was then "up-quenched" to a higher

temperature[14] and the ordering observed by measuring the increase in LEED beam intensity at the $p(2 \times 1)$ superlattice positions. The intensity was measured with a detector that subtended $1°$ at the sample. The substrate was cleaned in vacuum by annealing in O_2 with subsequent flashing to high temperature to remove the oxide.[15] Exposures were initially made at room temperature to correlate exposure and coverage. The evolution of the peak intensity of a superlattice reflection [the $(\frac{1}{2}, \frac{1}{2})$ beam] with exposure was used to fix the coverage. The point where the peak intensity first reaches its plateau value was chosen to correspond to $\theta = 0.5$. Sticking-coefficient measurements[16] were used to relate low-temperature exposures to coverage. Coverages could be determined to $\pm 20\%$ of the nominal coverage.

Figure 1(a) shows the evolution of order at the $p(2 \times 1)$ saturation coverage ($\theta = 0.5$), where only domains of the $p(2 \times 1)$ phase exist and cover the whole surface. We have plotted the square root
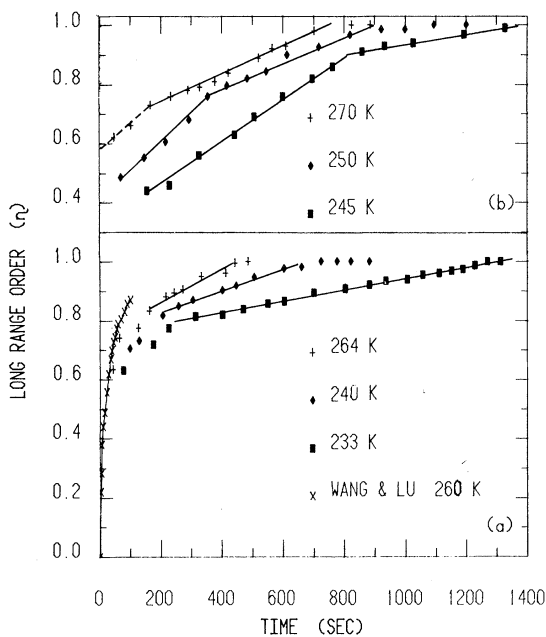

FIG. 1. Development of the long-range order parameter with time at several temperatures for W(110)p(2 $\times$1)-O: (a) one-phase region, $\theta = 0.5$; the data of Ref. 11 for W(112)p(2 $\times$1)-O are shown for comparison; (b) two-phase coexistence region, $\theta \approx 0.25$. Note that the temperature range for these data is slightly higher. At both coverages the data can be fitted by straight lines except at very short times. At sufficiently long times the order parameter reaches its maximum value and the growth rate goes to zero. See text for discussion.

of the intensity, which is taken to be proportional to the long-range order parameter,[17] η, versus time at several annealing temperatures. Figure 1(b) shows the same results at $\theta \approx 0.25$ where islands of $p(2 \times 1)$ phase coexist with a lattice gas. Several facts are apparent: (1) At both coverages there seem to be more than one time regime, in which the order parameter changes differently with time. (2) The rate of ordering depends significantly on coverage. (3) At both coverages the growth of the order parameter after an initial short time period can be fitted with straight lines, indicating a $t^{1/2}$ dependence for the change in average domain or island size.[18] (Obviously, at sufficiently long times, when the order parameter reaches a value of 1, the growth rate goes to zero.) (4) The growth is slower than that observed[11] for W(112)p(2 × 1)-O.

At $\theta = 0.5$, the coverage where only the $p(2 \times 1)$ phase can exist, the data can be fitted with a single straight line at all but short ordering times, indicating a single domain-growth mechanism that follows a $t^{1/2}$ dependence until the order parameter reaches its maximum value. Evidently the $p = 4$ degeneracy does not affect the time dependence of the domain growth. The limited data we have at short times indicate that the increase in the order parameter is more rapid than at longer times. On physical grounds, the influence of multiple ground states should be more apparent at long times than at short. This is found in calculations, which show a straight-line behavior at long times.[2,3,8-10] The high ordering rate at short times may be due to a rapid initial ordering process, such as elimination of very unfavorable boundaries or the diffusion into lattice-gas sites of atoms frozen during deposition into sites that are not lattice-gas sites. Multistage ordering is also found in calculations.[9,10] The growth is slower than for an equivalent $p = 2$ system, W(112)p(2×1)-O.[11]

At the coverage corresponding to two-phase coexistence, there appear to be three stages of ordering. Initially there is again rapid ordering, which may be due to a process similar to the one mentioned above. The second stage can be identified with growth of islands out of the disordered lattice gas, a process that will proceed until an equilibrium between islands and lattice-gas phase is reached. Because the data can be fitted by a straight line in this region, indicating $t^{1/2}$ dependence, this intermediate-time regime must reflect diffusion-limited island growth, i.e., the rate at which the islands grow is limited by dif-
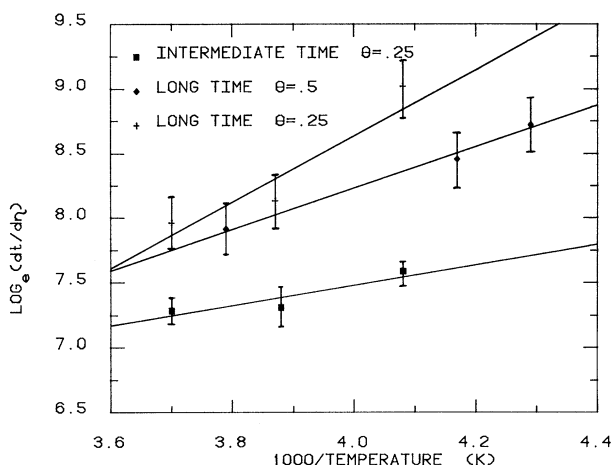
FIG. 2. Dependence of the slopes of the straight lines in Fig. 1 on inverse temperature, for three different ordering regimes (see text). The error bars reflect the uncertainty in the slopes of the lines in Fig. 1.

fusion to the island boundary.[14] The activation enthalpy for growth in this time regime should thus be related to an effective diffusional barrier for O on the W(110) surface. The other type of growth that could occur is reaction-limited island growth, i.e., the growth is limited by the incorporation rate of atoms at the island boundary. This can be shown to have a t dependence,[14] which is not observed. The third stage of ordering in Fig. 1(b) can be identified with coarsening, the growth of large islands at the expense of small ones. Coarsening can take place by atom exchange between islands or across possible antiphase domain boundaries within an island. Again a $t^{1/2}$ dependence is observed until the order parameter reaches its maximum value. The activation energy and frequency factors for the coarsening process may in general be different from those for island growth discussed above. In any case, it is apparent that the coarsening process is slower than the island growth process,

although both follow a $t^{1/2}$ dependence.

Activation energies and frequency factors for these ordering processes can be estimated from the data of Fig. 1. We define in each case zero time as the value where the extrapolation of the straight lines fitted to the data intercept the time axis. One can then write $\eta(t) = \alpha t$, where $\alpha = \nu \times \exp(-\Delta H/k_B T)$, ΔH is an activation enthalpy, and ν is a frequency factor. ΔH measures an effective activation barrier to ordering, for each process. In all the cases discussed here, it should reflect a diffusional barrier, because of the $t^{1/2}$ dependence. ν measures in essence the difference in atom flux coming to and leaving a domain or island. Its magnitude reflects the driving force for domain or island growth and the influence of the ground-state degeneracy. A small driving force implies that the differences in curvature of domain walls are small or that the boundary energy is not much larger than kT. The latter in turn implies that the boundaries are diffuse. A large degeneracy p makes ν small because it reduces the possibility of annihilation of boundaries. ΔH and ν can be determined by plotting $\ln[d\eta(t)/dt]$ vs $1/T$ (see Fig. 2). The results for the linear region in Fig. 1(a) and the two linear regions in Fig. 1(b) are given in Table I.

The values for both activation energies and frequency factors are too uncertain to permit the drawing of detailed conclusions. It does appear that the activation energies for the two processes that we have identified as domain growth or coarsening processes are similar to each other and somewhat different from that for the island growth process. In all cases, the ΔH values are smaller by about a factor of 5 than activation energies measured for diffusion of O on W(110).[19] This may imply that there is included in α a factor with a dependence on temperature that is opposite to that of the ΔH term. A simple possibility is a temperature-dependent concentration gradient of the diffusing O atoms at the island or

TABLE I. Activation energies and frequency factors for ordering of O on W(110).

	ΔH (eV)	ν (sec^{-1})
One-phase $p(2\times1)$ region, $\theta = 0.5$	0.17 ± 0.1	$0.4^{+40}_{-0.35}$
Coexistence region, $\theta \simeq 0.25$		
Long times	$0.24^{+0.05}_{-0.1}$	$8^{+80}_{-7.9}$
Intermediate times	0.07 ± 0.05	$0.01^{+0.4}_{-0.009}$

domain edge. A more detailed conclusion is not possible at this time. The frequency factors also appear small,[19] indicating that the driving force is not much larger than kT,[20] or that the influence of the degeneracy p is large. The net rate of incorporation of atoms into the ordered phase appears in any case to be small, leading to a picture of domains or islands that, although they may be quite large, have very diffuse, poorly defined boundaries.

In summary, we have presented results for the growth of islands and domains at two coverages for W(110)p(2×1)-O, a $p=4$ system. Growth proceeds according to $L(t) \propto t^{1/2}$ except perhaps during the earliest stages of growth. The growth is slower than that for a similar $p=2$ system.[11] A detailed comparison is impossible at this stage because our results describe the long-time behavior while those of Ref. 11 are for short times. Activation energies and frequency factors appear to be low compared to values for diffusion of O on W(110),[19] leading to the conclusion that the ordering is not described by a simple mass-transport phenomenon.

There is, finally, a possibility that the ground-state degeneracy in this system is 8 rather than 4. If one assumes that the O atoms sit in the threefold hollows in the W(110) surface there are four translationally equivalent sites rather than just two. The total degeneracy then becomes 8. If this is, in fact, the case, we have shown that a $t^{1/2}$ growth law dependence exists for a $p=8$ degeneracy.

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[1]P. S. Sahni, G. S. Grest, M. P. Anderson, and D. J. Srolovitz, Phys. Rev. Lett. 50, 263 (1983).

[2]P. S. Sahni, G. S. Grest, and S. A. Safran, Phys. Rev. Lett. 50, 60 (1983).

[3]A. Sadiq and K. Binder, Phys. Rev. Lett. 51, 674 (1983).

[4]P. S. Sahni and G. S. Grest, J. Appl. Phys. 53, 8002 (1982).

[5]T. Ohta, D. Jasnow, and K. Kawasaki, Phys. Rev. Lett. 49, 1223 (1982).

[6]P. S. Sahni and J. D. Gunton, Phys. Rev. Lett. 47, 1754 (1981).

[7]S. A. Safran, Phys. Rev. Lett. 46, 1581 (1981).

[8]P. S. Sahni, G. Dee, J. D. Gunton, M. Phani, J. L. Lebowitz, and M. Kalos, Phys. Rev. B 24, 410 (1981).

[9]I. M. Lifshitz, Zh. Eksp. Teor. Fiz. 42, 1354 (1962) [Sov. Phys. JETP 15, 939 (1962)].

[10]S. M. Allen and J. W. Cahn, Acta Metall. 27, 1085 (1979).

[11]G.-C. Wang and T.-M. Lu, Phys. Rev. Lett. 50, 2014 (1983).

[12]E. Domany, M. Schick, and J. S. Walker, Phys. Rev. Lett. 38, 1148 (1977).

[13]T.-M. Lu, G.-C. Wang, and M. G. Lagally, Phys. Rev. Lett. 39, 411 (1977), and Surf. Sci. 92, 133 (1980); M. G. Lagally, T.-M. Lu, and G.-C. Wang, in Ordering in Two Dimensions, edited by S. Sinha (Elsevier, New York, 1980).

[14]J. H. Perepezko, J. T. McKinney, P. K. Wu, and M. G. Lagally, to be published.

[15]J. A. Becker, E. J. Becker, and R. G. Brandes, J. Appl. Phys. 32, 411 (1961).

[16]C. Kohrt and R. Gomer, J. Chem. Phys. 32, 3283 (1970).

[17]This assumes that the islands or domains are randomly arranged and have a distribution of sizes, and that their interference therefore makes a negligible contribution to the diffracted intensity. See T.-M. Lu, L.-H. Zhao, M. G. Lagally, G.-C. Wang, and J. E. Houston, Surf. Sci. 122, 519 (1982).

[18]η is proportional to the area of ordered regions; hence a linear relationship between η and t indicates $L(t) \propto t^{1/2}$.

[19]J.-R. Chen and R. Gomer, Surf. Sci. 59, 413 (1979).

[20]Previous estimates of the net cohesive energy for $p(2 \times 1)$ oxygen islands on W(110) are 0.07 eV, approximately $3kT$. See Ref. 13.