Scaling in the Ordering Kinetics of a Chemisorbed Overlayer: W(110)-$p(2\times1)$O

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Measurements of the ordering kinetics for the $p(2\times1)$ chemisorbed layer on W(110) have been made by LEED angular-profile analysis at coverages at which the $p(2\times1)$ structure exists as a single phase and coexists with disordered lattice gas. It is shown that the growth of ordered domains proceeds with a power-law time dependence, consistent with calculations, and obeys a scaling relationship. In the coexistence region, a bimodal size distribution is observed.

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Recently there has been intense theoretical interest in extending thermodynamic studies of two-dimensional phases to the dynamics of ordering of a phase as it approaches equilibrium from an initial nonequilibrium disordered state.[1-5] The reason for this interest is the expectation that questions of universality, conservation laws, and, eventually, interaction energies between adatoms in a 2D phase can be addressed from its ordering behavior. A general prediction of models of growth dynamics[1-7] is that the growth of the average ordered-domain size, L, obeys a power law

$$L=A(T)t^x \tag{1}$$

for a variety of conditions on the coverage, the time, and the symmetry of the overlayer. Here $A(T)$ is a rate coefficient that depends on temperature and t is the ordering time. The exponent x depends only on conservation laws that are operative and on universal parameters such as the number of degenerate low-temperature ordered phases that can coexist. Monte Carlo modeling further indicates that the growth obeys a scaling relationship, i.e., that the domain structure of the system at some later time is similar to that at an earlier time after distance has been rescaled. Self-similarity in the growth implies scaling of the autocorrelation function of the structure and hence also of its Fourier transform, which is the angular distribution of intensity in beams diffracted from the 2D phase,

$$S(\mathbf{k},t)/I_p=F(\mathbf{k}/w), \tag{2}$$

where S is the angular profile for a given reflection defined by the momentum transfer wave vector $\mathbf{k}$, t is the time, I_p is the peak intensity, and F is some characteristic function that depends on $\mathbf{k}$ and on the full width at half maximum (FWHM), w, of the profile. The angular distribution reflects the mean domain size and the size distribution. Scaling implies that, although the average domain size changes with time, the functional form of the size distribution does not.

The few experimental studies of growth dynamics of 2D phases generally have been limited to evaluating the growth law from diffraction measurements of the change of the peak intensity of superlattice beams with time.[8-11] In order to test for self-similarity and scaling and to measure the domain-size distribution, angular profiles of beams must be measured. In this Letter we present LEED results for the growth of the $p(2\times1)$ domains in W(110)-$p(2\times1)$O at two coverages, $\theta=0.5$ and $\theta=0.25$. Schematic diagrams of the order existing at some intermediate time in the ordering process for these two situations are shown in Fig. 1. Ordering processes in these two regimes can be fundamentally different, involving domain growth at $\theta=0.5$ and nucleation, growth, and coarsening at $\theta=0.25$. We measure both the LEED peak intensity and angular profile of $p(2\times1)$ superlattice reflections to investigate the growth law and check for scaling behavior.

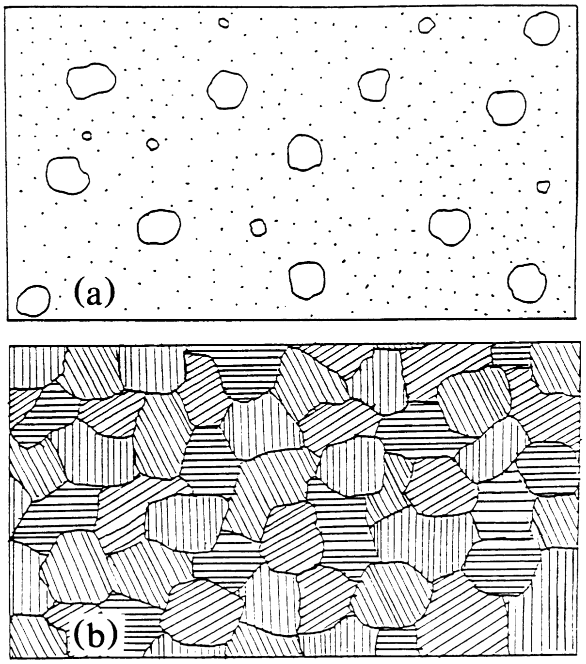

FIG. 1. Schematic diagrams of order existing at some intermediate time in the ordering process for (a) two-phase coexistence and (b) a single phase.

The experiment is carried out in a LEED diffractometer at base pressures in the high 10^{-11}-Torr range. The instrument response, expressed in terms of the FWHM of the narrowest profile that the instrument can measure, is 0.04 of the Brillouin zone at the diffraction conditions of the experiment and is taken into account in all data analysis. The initial condition for the growth-dynamics experiments is simulated[8,9] by first cooling the W(110) surface to $\simeq 200$ K and then dosing the surface with O. Its mobility at this temperature is effectively zero,[9] and it is assumed that the distribution of O on the surface represents an infinite-temperature configuration. The system is subsequently rapidly raised to and held at a temperature where O atoms are mobile and the intensity increase of superlattice beams monitored. Angular profiles are measured at regular intervals during the annealing process. The oxygen coverage is determined by monitoring the $(0, \frac{1}{2})$ beam intensity as a function of exposure at 300 K and searching for its maximum, which indicates $\theta = 0.5$.[12] The coverage-exposure relationship at 200 K is established by use of the results at 300 K and sticking-coefficient measurements at 200 K.[13] The validity of this procedure was checked by subsequently annealing the layer at 300 K and comparing the peak intensity and angular profile of the $(0, \frac{1}{2})$ beam to those obtained for exposure at 300 K. Although the absolute coverage above $\theta = 0.45$ is difficult to determine accurately in this manner, because the sticking coefficient drops rapidly above this coverage, structural phenomena occurring[14] just above $\theta = 0.5$ aid in fixing $\theta = 0.5$.

Measurements were made from about 10 sec after the initiation of the step in temperature to 900 sec thereafter, and repeated for seven temperatures between $\simeq 260$ and $\simeq 300$ K. Below 260 K the ordering is too slow to observe reliably. Within this temperature range, we observe at both coverages a power-law growth of the ordered domains for approximately 600 sec, after which the growth begins to slow, indicating that a second mechanism for ordering is becoming important. Above 300 K, the ordering is too rapid to identify unequivocally the mechanism we observe at lower temperatures. At $\theta = 0.5$, the existence of power-law growth is determined from a plot of ln(peak intensity) versus ln(time), which shows a series of parallel straight lines. The slope of these lines is $2x$, where x is the growth exponent. The factor of 2 arises because the peak intensity is proportional to the square[3,9b] of the mean domain. Figure 2 shows a plot of the peak intensity for $\theta = 0.5$ at several temperatures plotted versus t^{2x}, where the growth exponent[15] $x = 0.28 \pm 0.02$. The lines are straight, go through the origin, and have slopes that are proportional to $A(T)$.

Angular profiles corresponding to this ordering process are measured at several times and fitted with a model calculation of domain size and size distribution.[14] We find at $\theta = 0.5$ a narrow Gaussian domain-size distribution, changing in mean diameter from $\simeq 9$ to 15Å as the ordering proceeds. Such domains contain on the average of 5 to 15 O atoms and are thus still very small in this time regime. Domain sizes for the fully annealed structure are an order of magnitude larger. By plotting ln(mean domain size) versus ln(time) at several temperatures, we find a growth exponent of 0.28 ± 0.02, in agreement with the result for the peak intensity.

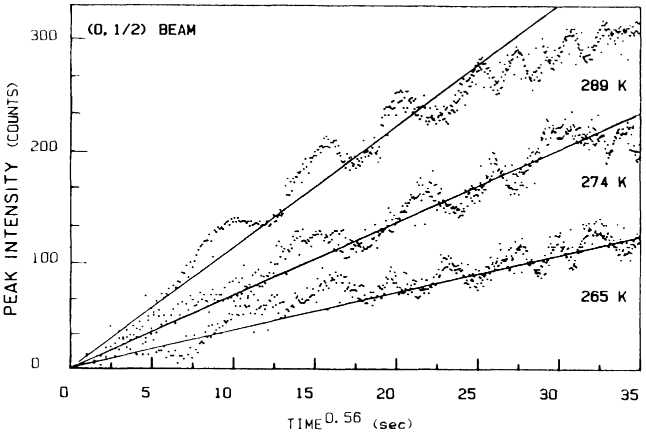

FIG. 2. Demonstration of power-law growth at $\theta = 0.5$ from peak intensities. The peak intensities at three temperatures are plotted vs t^{2x}, with $x = 0.28$. The slopes of the lines are proportional to the rate constant $A(T)$.

To consider scaling in the growth, angular profiles after deconvolution[16] of the instrument response function are replotted according to Eq. (2) with their FWHM's normalized. The results for one temperature are shown in Fig. 3(a). Similar agreement is achieved for the other temperatures. It is evident that self-similar growth occurs in the domains at $\theta = 0.5$ for $260 < T < 300$ K. This is, in fact, a necessary condition in view of the observations of power-law growth and nonvarying domain-size distribution with time.

Theories and Monte Carlo modeling for ordering dynamics in a one-phase region[1-4,6a] suggest that the growth exponent depends on ground-state degeneracy p and is $\frac{1}{2}$ or lower. Available results for the symmetry represented by W(110)-$p(2\times1)$O and $p = 4$ predict[3] $x = 0.35$. There is evidence[9b,9c] that $p = 8$ in this system. Thus the theoretically expected exponent may even be smaller than 0.35. To our knowledge, no calculation has been made for $p = 8$. The scaling function, F, that we observe is a Gaussian, in agreement with Ref. 4.

The experimental situation at $\theta = 0.25$, where the overlayer coexists at equilibrium as $p(2\times1)$ islands and disordered lattice gas (Fig. 1), is more complicated. The sequence of mechanisms of ordering of a quenched disordered lattice gas in a two-phase region is expected to be nucleation, growth by monomer addition from the supersaturated lattice gas phase, and subsequently coarsening

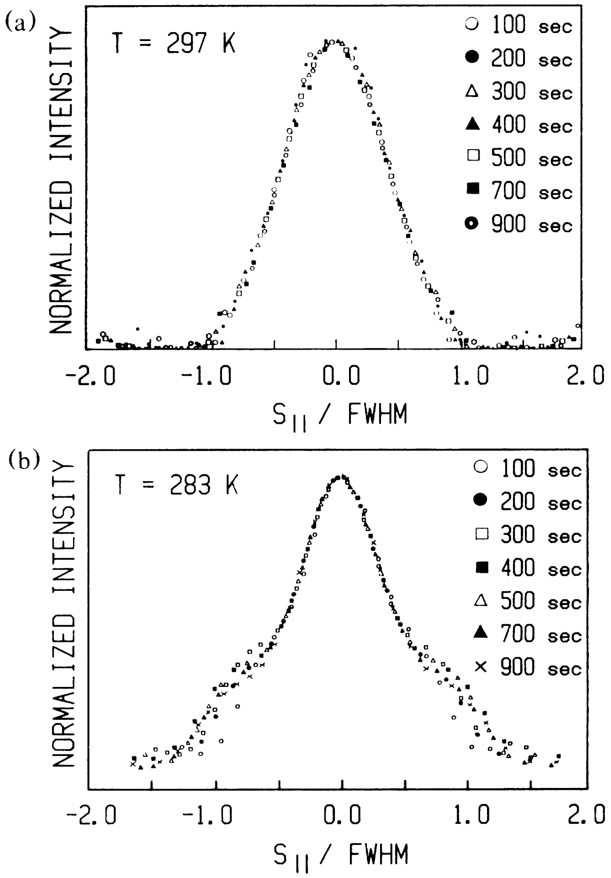

FIG. 3. Demonstration of scaling in the growth of $p(2\times1)$ domains at (a) $\theta=0.5$ and (b) $\theta=0.25$. Angular profiles of the $(0,\frac{1}{2})$ superlattice beam at a fixed temperature and several times are plotted with their widths scaled according to Eq. (2). The profile in (b) consists of a broad and a narrow Gaussian, indicating a bimodal distribution of island sizes.

(growth of large islands at the expense of small ones) to reduce boundary energy. We have investigated ordering kinetics at this coverage in the same manner as indicated for $\theta=0.5$, by measuring angular profiles of a superlattice diffracted beam at various times and temperatures and fitting the profiles. The profiles always show a narrow and a broad component, each of which can be fitted with a Gaussian[14], indicating that the island-size distribution is bimodal, consisting of large and small islands that each are Gaussian distributed about their mean sizes. Figure 3(b) shows that, to a good approximation, both components of the profile scale with a single scaling parameter. Over the measurement time and temperature range investigated, the mean size of the smaller islands changes from $\simeq 7$ to 15 Å with a standard deviation of $\simeq 3$ Å, the ratio of mean sizes of large and small islands is $\simeq 3$, and the density of smaller islands is $\simeq 15$ that of the larger ones. If one accepts that the profiles scale, then the peak intensity can be used[14] to determine the growth exponent, giving $x=0.28\pm0.05$, very similar to the value at $\theta=0.5$.

The prevailing theory of growth by coarsening in a two-phase coexistence region is that of Lifshitz and Slyozov,[6b] for a model of $p(1\times1)$ phase and lattice gas, giving $x=\frac{1}{3}$. The same exponent is found even if the concentration of ordered phase is large.[5,7] No theory exists specifically for the present system, which is not $p(1\times1)$ and has large degeneracy. It seems reasonable that the growth exponent will be lower than $\frac{1}{3}$. Scaling is usually observed in the calculations. The experiment indicates that scaling is obeyed; however, we observe a bimodal size distribution. The origin of a bimodal distribution may be fundamental or a consequence of defects. One can imagine that islands with a critical small size can decorate surface defects. However, it is not obvious why such islands should grow, but more slowly than the larger islands. On the other hand, if some form of diffusion zone mechanism[17] is operative, where all atoms within a certain range preferentially diffuse to one island, then a size distribution that has a component of large, nearly equal-sized islands and another component of much smaller islands may be possible.[18]

At late times for both coverages, the growth begins to slow at sufficiently long times, indicating that the exponent is dropping. Although it cannot be conclusively excluded that defects cause[19] the slowing down, we observe a temperature-dependent average domain size at which the growth slows, which suggests that defects are not responsible.[14]

Finally, we consider activation energies for these ordering processes. From data such as those shown in Fig. 2 and the assumption that $A(T)$ in Eq. (1) has Arrhenius-type behavior, one can directly extract an activation energy. Doing so gives $\Delta H=0.16\pm0.03$ eV for the process at $\theta=0.5$ if the peak intensities are used and 0.17 ± 0.5 eV if the mean sizes determined from the profiles are used. This consistency is important and reflects the scaling: If the size distribution function changes over the course of the ordering, the peak intensity is not a meaningful quantity in terms of growth exponent or activation energy. At $\theta=0.25$ the value is $\Delta H=0.15\pm0.06$ eV, very similar to the value at $\theta=0.5$. How are these activation energies to be interpreted? In the Lifshitz-Slyozov theory, $A(T)\propto D^{1/3}$, where D is the diffusion coefficient. If one accepts that this theory is applicable to our $\theta=0.25$ data, then one obtains an activation energy for diffusion of O atoms on W(110) of $\Delta H_{\text{diff}}=0.45$ eV, somewhat less than the 0.6 eV quoted by Chen and Gomer.[20] Our process is a nonequilibrium process, in contrast to that measured by Gomer, and it is not surprising that the diffusion coefficient in our case should be less, because on the average, a diffusing O atom finds itself in a more unfavorable environment, where it sees more repulsive interactions from adjacent O atoms, than in the equilibrium case. At $\theta=0.5$ using the experimentally determined growth exponent, one obtains $\Delta H_{\text{diff}}\simeq 0.5$ eV. Its similarity to the value at

$\theta=0.25$ can be understood on the basis of the similar average interactions that a randomly placed atom at $\theta=0.25$ and at $\theta=0.5$ sees.[14]

In summary, we have observed scaling behavior in the growth of a chemisorbed submonolayer at coverages corresponding to one-phase and two-phase coexistence regions. We obtain very similar growth exponents in the two cases, although the thermodynamic final states are different. We observe a bimodal size distribution for growth in the two-phase region, with apparent scaling in the growth in both components. We have determined activation energies for the process, which can be interpreted in terms of a nonequilibrium diffusion coefficient for O on W(110).

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