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A. Autorenverzeichnis

Ordering Kinetics for O on W(110)*)

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Chemical Kinetics / Critical Phenomena / Electron Diffraction / Phase Transitions / Surfaces

An analysis of peak-intensity-vs-time data for LEED from W(110)$p(2\times1)$-O at saturation coverage is made to emphasize early times. From this analysis an exponent $x \simeq 0.33$ for the growth of the average size of ordered domains is extracted. Experimental evidence for a ground-state degeneracy $p = 8$ in this system is presented, supporting the existence of slow domain growth that is suggested by the growth exponent. The relationship to recent theoretical results is discussed.

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Introduction

The ordering of two-dimensional (2-D) overlayers reflects a host of fundamental phenomena, such as adsorbate interactions, diffusion barriers, the mode of growth, substrate and overlayer symmetry, the influence of island boundaries or domain walls, and the existence of substrate defects. As a consequence, the kinetics of ordering of 2-D systems has been the subject of recent intense interest [1 – 10]. A measure of the growth kinetics is the increase in average size of ordered domains with time. If one assumes that a growth law $\langle L\rangle \alpha t^x$ is operative, then the exponent x defines this rate of growth. The growth law $\langle L\rangle \alpha t^x$ follows from the scaling hypothesis. The determination of x under different conditions and its relationship to the number of ground states of the system have been of particular concern. The ordering of O on W(110) encompasses several of the features that are at the core of a detailed understanding of growth kinetics of 2-D systems. There are at least two ordered structures of O on W(110), both one-phase and coexistence regions are easily accessible in temperature, the ground state of the $p(2\times 1)$-O structure is highly multiply degenerate ($p = 8$ for the most probable adsorption site and $p = 4$ for other sites), and some estimates of the adatom interactions are available from fits [11 – 13] to the experimentally determined phase diagram [14]. Both the W(110)$p(2\times 1)$-O ($\theta_{sat} = 0.5$) and W(110)$p(2\times 2)$-O ($\theta_{sat} = 0.75$) phases belong to the xy model with cubic anisotropy if $p = 4$ [15].

Ordering kinetics of two-dimensional systems are most easily studied with a surface-sensitive diffraction technique. Because a large area of the sample surface is illuminated coherently, diffraction provides a statistical average of the order that is present at the instant the diffraction measurement is made. Measurements are invariably made on a quenched-in, disordered phase that is subsequently rapidly raised to and held at a particular annealing (growth) temperature. Low-energy electron diffraction (LEED) is the most prevalent technique in use for these purposes [6 – 10].

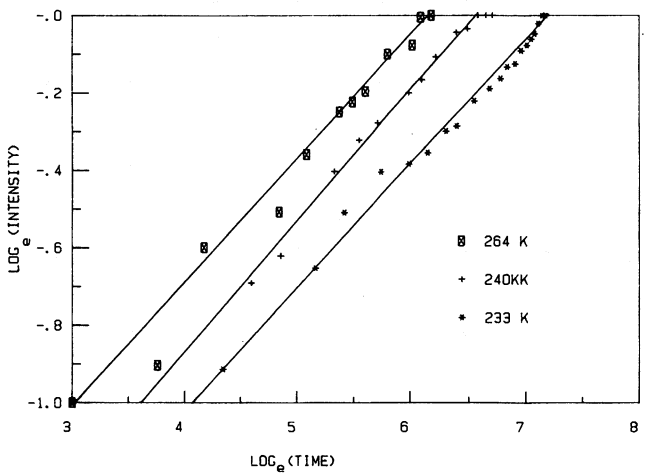

Fig. 1
Log of the peak intensity of the (1/2, 1/2) diffracted beam from W(110)$p(2\times 1)$-O at saturation coverage vs log (time) for three different annealing temperatures. The nearly parallel straight lines indicate that the data can be fitted using a single domain growth mechanism. The average slope of the lines is 0.66

From the diffraction measurement, the average size of ordered regions can in principle be determined both from the angular profile or from the peak intensity of diffracted beams from the overlayer phase. All but the most recent measurements have considered only the peak intensity. We discuss here a reinterpretation of peak intensity-vs-time data for W(110)$p(2\times 1)$-O that emphasizes early-time behavior. We discuss possible difficulties with this interpretation that apply also to others based on peak-intensity measurements. We also present new experimental evidence that suggests that the ground state degeneracy for W(110)$p(2\times 1)$-O is $p = 8$.

Results

In the earlier analysis of the growth of the saturation-coverage W(110)$p(2\times 1)$-O phase (prepared by adsorbing O at LN_2 temperatures and then annealing at higher temperature) [7] emphasis on long-time behavior required a fit with two different ordering mechanisms. If the long-time behavior is deemphasized relative to the short-time behavior (accomplished by plotting the data on a log-log plot and using the best slope to fit the data), it is evident that a single ordering mechanism suffices. This is shown in Fig. 1, in which $\log J_p$, the measured peak intensity, is plotted vs. $\log t$, the time, for three different temperatures. The average slope of these curves gives

$$J_p \alpha t^{0.66} . \tag{1}$$

In order to extract the time dependence of an average domain size from the peak intensity (i.e., the exponent x) some assumption needs to be made about how the peak intensity reflects the average domain size. If one assumes that there are $N = M_1 \times M_2 = L_1 a \times L_2 b$ atoms in a 2-D domain and all atoms contribute coherently, then the peak intensity scattered from this domain is

$$I_p \alpha N^2 |f|^2 = M_1^2 M_2^2 |f|^2 . \tag{2}$$

If R domains of this kind scatter incoherently, then

$$I_p \alpha R \langle L\rangle^4 . \tag{3}$$

This is the relation that has been used previously [6, 7]. However, in this result the coverage is not conserved as the domains grow. Furthermore, an incoherent superposition of scattering amplitudes from different domains can not be justified because, if one assumes ordered domains of adsorbed species on a well-ordered substrate the atoms all contribute coherently. A coherent superposition with conserved coverage gives

$$I_p \alpha \langle L\rangle^2 . \tag{4}$$

This can easily be seen as follows. Consider the diffuse intensity integrated over a Brillouin zone, which is equal to N, the total number of overlayer atoms, and thus to the coverage θ:

$$\theta \alpha N = \int_{B.Z.} I(S)\,dS \sim w^2 I_p , \tag{5}$$

where w, the width of the diffracted-beam profile, is the inverse of the average domain diameter $w \sim 1/\langle L\rangle$. If one assumes the coverage is conserved during the ordering process it is clear that Eq. (4) obtains directly.

We have neglected here possible multiple-scattering effects and a possibility that the atoms in the domain walls may be displaced from lattice sites and therefore do not contribute coherently to the intensity. This effect would simulate a coverage that is not constant

in time. In that case, a value somewhere between the above limits probably results, but it is usually assumed that this situation does not occur. It should be noted that limited instrument response does not at all affect these arguments, i.e., one can not assume incoherent superposition as a result of a limited capability of the instrument to resolve long-range correlations (i.e., a small "transfer width") [16]. From Eqs. (1) and (4) then, $\langle L\rangle \alpha t^{0.33}$, i.e., $x = 0.33$.

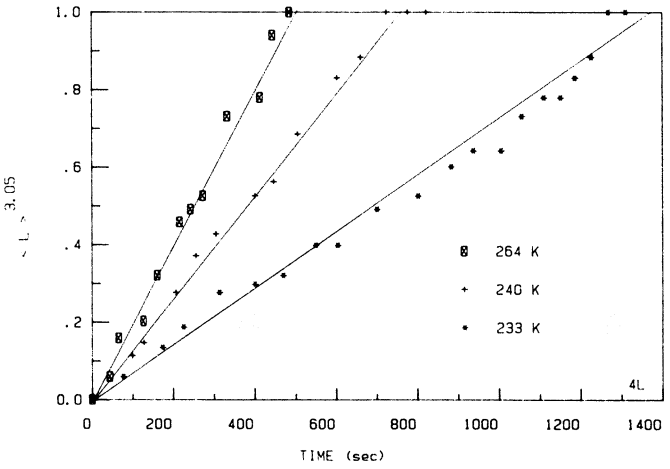

Fig. 2
Domain growth vs. time. The data of Fig. 1 are replotted assuming the average linear dimension $\langle L\rangle$ of domains is proportional to the square root of the peak intensity

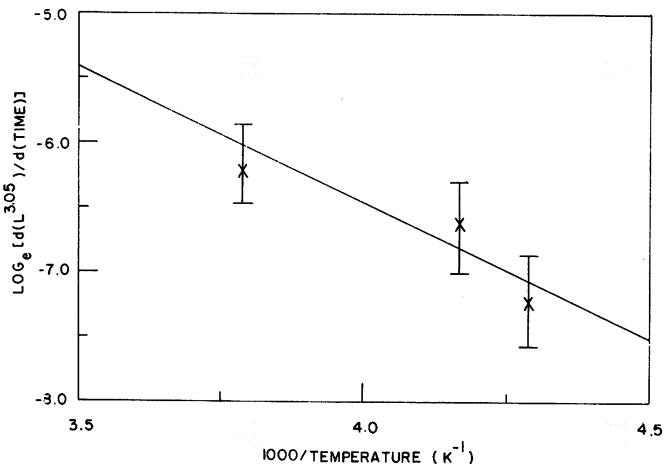

Fig. 3
Activation energy for the ordering process indicated in Fig. 2. The slopes of the lines in Fig. 2 are plotted vs. inverse temperature. The fit gives an activation energy of 0.15 ± 0.1 eV and a preexponential factor of $6.8 \cdot 10^{-1\ \pm 2}$ sec^{-1}

Discussion

Fig. 2 shows the data of Fig. 1 plotted so that the time axis is linear. It clearly shows that a single process suffices to explain the growth behavior over the range over which the data were taken. If one assumes that

$$\langle L\rangle^{1/x} = r(T)t = r_0 e^{-\Delta H/kT} t, \tag{6}$$

then plotting the log of the slopes of the lines in Fig. 2 vs. inverse temperature gives the activation energy for the change in $\langle L\rangle^{3.05}$. This is shown in Fig. 3. We have no physical interpretation at present for this activation energy. However, one can expect it to reflect the difficulty with which boundaries are moved in the overlayer film. It is clear that one should not expect the value to reflect a simple diffusional barrier [17,18].

The value obtained in Fig. 2 is very close to that of Sadiq and Binder [1], who calculated ordering for a system analogous to W(110)$p(2\times 1)$-O at saturation coverage, using a ground state degeneracy of $p = 4$. We present evidence here that $p = 8$ in W(110)$p(2\times 1)$-O. This is done by evaluating the development of the diffuse intensity as a function of coverage for an overlayer that is assumed to be a random lattice gas. This is achieved by depositing O at low enough temperatures so no ordering occurs (i.e., no superlattice reflections appear with time). The overlayer atoms are all assumed to occupy lattice gas sites. These two statements are equivalent to saying that there is sufficient driving force for atoms to assume regular lattice sites, but insufficient activation energy for them to migrate between sites to form an ordered structure. In that case, the diffuse intensity, I_D, is [19]

$$I_D \alpha \theta(1-\theta), \tag{5}$$

where θ is the coverage, and the 1 implies that saturation is one monolayer. If there is only one possible energetically equivalent lattice site per unit mesh, the diffuse intensity has a maximum at $\theta = 0.5$. The decrease beyond this point is due to accidental correlations between atoms placed randomly in lattice sites. At $\theta = 1$, of course, no disorder diffuse intensity can be present, because all sites are occupied [19]. If these are two possible energetically equivalent sites in the unit mesh then the diffuse intensity will not have a maximum at $\theta = 0.5$, but rather only at $\theta = 1$. In other words, accidental correlations can not reduce the diffuse intensity. In W(110) the two three-coordinated sites on either side of the long-bridge site are equivalent. Only one can be occupied in each unit mesh, but different unit meshes can have one or the other occupied. This site would produce a ground state degeneracy of $p = 8$, two translational antiphase domains and two rotational antiphase domains for each possible three-coordinated site. This site is the only one on W(110) for which $p = 8$, but is the site that is found in LEED calculations [20] to be the preferred one. Fig. 4 shows the diffuse intensity vs. exposure. The measurement was made with a fluorescent screen subtending a solid angle of approximately 10°, at sufficiently low energy so that the (00) and (10) fundamental reflections just fall off the sides of the screen. The screen thus measures a reasonable fraction of one Brillouin zone. O was adsorbed at LN_2 temperatures and the background intensity monitored as a function of coverage. Fig. 4 also shows the diffuse intensity measured for W(112) [21], for which $p = 2$ and only one site per unit mesh is possible.

One of the important questions in theoretical growth dynamics studies is the influence of ground state degeneracy. Our present interpretation provides good agreement for the growth exponent x with the calculation of Sadiq and Binder

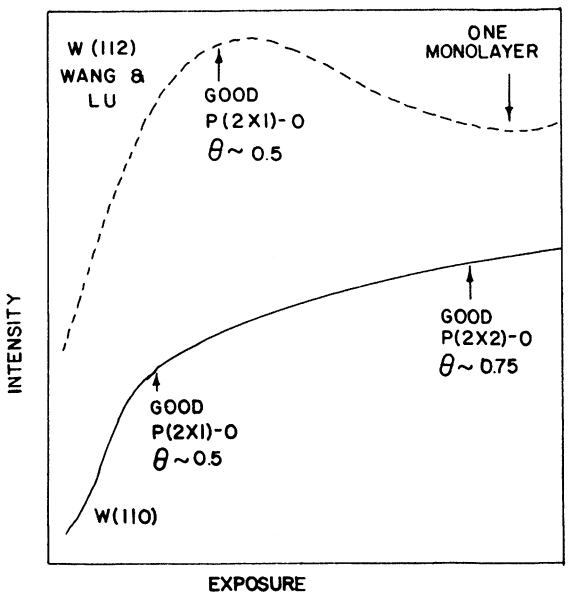

Fig. 4
Diffuse intensity vs. exposure for 0 adsorption on two surfaces of W at temperatures below which ordering occurs. Dashed line: O on W(112) [21]. Solid line: O on W(110). The arrows indicate exposure values at which optimum superlattice patterns are observed for adsorption at higher temperatures. The ground state degeneracy influences the position in exposure of maximum diffuse intensity. If $p = 4$ in O/W(110), a peak in the diffuse intensity should occur in the vicinity of $\theta = 0.5$. The absence of such a peak implies that $p = 8$. For O/W(112) ($p = 2$) a peak is observed at the appropriate coverage

[1], which was done for $p = 4$. This would, on the surface, suggest that ground-state degeneracy is not very important in influencing the growth exponent in this system. A possible explanation is that, although the ground state is eight-fold degenerate, only the four-fold degeneracy is effective, because the oxygen atom cannot occupy both three-fold sites in the unit cell. However, this conclusion can not be reliably drawn even in this system, and certainly not in general, because a number of other factors can affect the growth exponent, including the temperature at which growth occurs [1], coverage less than saturation [22], substrate defects, and the assumption that all atoms are in lattice sites. No definitive conclusion can therefore be drawn at this time.

Summary

We have reevaluated data for the LEED peak intensity from $p(2\times1)$ superlattice beams in the ordering of O on W(110) and have found that a single growth exponent of $x = 0.33$ fits the data over the time range that was measured. This agrees closely with theoretical results [1]. The ground state degeneracy chosen in the theory was $p = 4$. We have shown that $p = 8$ in the physical case. To check the influence of ground state degeneracy in this system, it is suggested that identical Monte-Carlo calculations be performed for $p = 4$ and $p = 8$.

In this analysis, we have used the peak intensity of the (1/2, 1/2) superlattice beam. No account was taken of the instrument response function, (i.e., J_p in Eq. (1) was assumed to be I_p in (Eq. (4)) an approximation that is equivalent to assuming that the island size is always small relative to the maximum distance that the instrument can resolve, so that the instrument response function is a negligible part of the measured profile. Initial measurements [18] indicate that the island size at low annealing temperatures is in fact of the order of 10–20 atoms in any direction, even for very long ordering times. Such small sizes make the neglect of the instrument response function a reasonable approximation. On the other hand, they also suggest some kinetic limitation to continued growth, such as substrate defects or domain wall interference.

Finally, use of the peak intensity in this simple way assumes the validity of the kinematic approximation. However, it has been shown that the peak intensity may be quite sensitive to multiple-scattering effects [23]. A far more reliable method for evaluating the growth of chemisorbed overlayers is from angular profiles of the superlattice beams [24]. Such work is in progress on this system.

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References

[1] A. Sadiq and K. Binder, J. Statistical Phys. *35*, 617 (1984); Phys. Rev. Lett. *51*, 674 (1983).
[2] J. D. Gunton, M. San Miguel, and P. S. Sahni, in: Phase Transitions and Critical Phenomena, Vol. 8, p. 267, eds. C. Domb and J. L. Lebowitz, Academic Press, New York 1983.
[3] P. S. Sahni, D. J. Srolovitz, G. S. Grest, M. P. Anderson, and S. A. Safran, Phys. Rev. *B28*, 2705 (1983); G. S. Grest, D. J. Srolovitz, and M. P. Anderson, Phys. Rev. Lett. *52*, 1321 (1984).
[4] E. T. Gawlinski, M. Grant, J. D. Gunton, and K. Kaski, Phys. Rev. *B31*, 281 (1985); K. Kaski, M. D. Yalabik, J. D. Gunton, and P. S. Sahni, Phys. Rev. *B28*, 5263 (1983); J. Vinals and J. D. Gunton, Surf. Sci. *157*, 473 (1985).
[5] G. F. Mazenko and O. T. Valls, Phys. Rev. *B27*, 6811 (1983); *B30*, 6732 (1984).
[6] G.-C. Wang and T.-M. Lu, Phys. Rev. Lett. *50*, 2014 (1983).
[7] P. K. Wu, J. H. Perepezko, J. T. McKinney, and M. G. Lagally, Phys. Rev. Lett. *51*, 1577 (1983).
[8] R. J. Behm, G. Ertl, and J. Wintterlin, this conference.
[9] W. Witt and E. Bauer, this conference. W. Witt, Ph. D. Dissertation, Univ. Clausthal 1985.
[10] G. Ertl, this conference. G. Ertl, P. R. Norton, and J. Rustig, Phys. Rev. Lett. *49*, 177 (1982).
[11] W. Y. Ching, D. L. Huber, M. Fishkis, and M. G. Lagally, J. Vac. Sci. Technol. *15*, 653 (1978).
[12] E. D. Williams, S. L. Cunningham, and W. H. Weinberg, J. Chem. Phys. *68*, 5 (1978).
[13] M. Tringides and R. Gomer, Surf. Sci. *145*, 121 (1984).
[14] T.-M. Lu, G.-C. Wang, and M. G. Lagally, Phys. Rev. Lett. *39*, 411 (1977); G.-C. Wang, T.-M. Lu, and M. G. Lagally, J. Chem. Phys. *69*, 479 (1978); M. G. Lagally, T.-M. Lu, and G.-C. Wang, in: Ordering in Two Dimensions, p. 113, ed. S. Sinha, Elsevier, New York 1980.
[15] E. Domany, M. Schick, J. S. Walker, and R. B. Griffiths, Phys. Rev. *B18*, 2209 (1978).
[16] T. M. Lu and M. G. Lagally, Surf. Sci. *99*, 695 (1980); G. Comsa, Surf. Sci. *81*, 57 (1979).
[17] J. R. Chen and R. Gomer, Surf. Sci. *79*, 412 (1979); R. Butz and H. Wagner, Surf. Sci. *63*, 448 (1977); M. Tringides and R. Gomer, Surf. Sci. *155*, 254 (1985).
[18] P. K. Wu, M. Tringides, W. Moritz, and M. G. Lagally, in preparation.

[19] Although the dependence on θ is as indicated in Eq. (5), the actual situation is somewhat more complex. A more detailed treatment will appear elsewhere. W. Moritz, P. K. Wu, and M. G. Lagally, in preparation.
[20] M. A. Van Hove and S. Y. Tong, Phys. Rev. Lett. *35*, 1092 (1975).
[21] G.-C. Wang, personal communication, see also Ref. [6].
[22] K. Binder, this conference and personal communication.
[23] W. Moritz and M. G. Lagally, Phys. Rev. Lett. *56*, 865 (1986); H. Jagodzinski, Z. Naturforsch. *37a*, 1103 (1982).
[24] W. Moritz and M. G. Lagally, in preparation. H. Jagodzinski, W. Moritz, and D. Wolf, Surf. Sci. *77*, 233 (1978); W. Moritz, H. Jagodzinski and D. Wolf, Surf. Sci. *77*, 249 (1978); W. Moritz, in Inst. Chem. Conf. Ser. *41*, 266 (1978).

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