Order-Disorder Transition and Adatom-Adatom Interactions in a Chemisorbed Overlayer: Oxygen on W(110)*

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The intensity and angular width of superlattice reflections in low-energy electron diffraction from W(110)$p(2\times1)$-O are measured as the overlayer disorders. The width of the reflections increases with temperature, indicating a shrinking of island size. An adatom-adatom interaction energy is determined for this system by using a short-range-order model and calculating the diffracted intensity from a chain of atoms.

The description of the surface chemical bond for simple adsorbate systems is the necessary first step to studying more complex systems such as surface reactions. Whereas for a single chemisorbed atom, quantities such as the binding energy, activation energy for diffusion, adsorbate-substrate (A-S) force constant, and equilibrium site and spacing are simply related to the A-S interaction potential, for more than one atom, adsorbate-adsorbate (A-A) interactions seriously complicate the interpretation. It thus seems imperative to investigate in detail such interactions. This Letter reports a measurement of a lateral-interaction energy by studying the reversible thermal disordering of the chemisorption system W(110)$p(2\times1)$-O.

It has long been recognized[1] that lateral interactions are important. One can frequently tell from the development of the low-energy–electron-diffraction (LEED) pattern as a function of coverage whether lateral interactions in particular directions are attractive or repulsive. However, the magnitude of these interactions is much harder to obtain. In principle, the change of the heat of adsorption with coverage should give a measure of the A-A interaction energies. Some success has been achieved in this manner if the A-A interactions are strictly repulsive.[2] However, if attractive interactions are present, growth of ordered islands takes place by the addition of atoms at the island boundaries and the heat of adsorption becomes constant at very low coverages, i.e., after the size of the island exceeds a few atomic diameters. In this case, the lateral-interaction energies can sometimes be obtained by observing the diffraction from an ordered layer as it undergoes reversible thermal disordering. This is, of course, well known in the theory of ordered alloys, but has been almost completely ignored for surfaces.[3]

We have measured the order-disorder transition in W(110)$p(2\times1)$-O in order to extract a lateral-interaction energy. This system has been studied extensively.[4] Some relevant results are as follows: (1) Oxygen chemisorption below 1000°K to the half-monolayer coverage does not reconstruct W(110); hence the O atoms sit on top of W.[5] (2) Observation of the diffraction as a function of coverage shows sharp superlattice beams even at lowest coverages, indicating that ordered islands nucleate randomly on the surface and grow rapidly by the addition of atoms at their boundaries.[6] The final $p(2\times1)$ structure consists of domains of doubly spaced close-packed rows parallel to $\langle111\rangle$ directions. The double spacing indicates a nearest-neighbor (NN) repulsion, but in order to form islands, a next-nearest-neighbor (NNN) attraction is also required. Along the close-packed O rows, the interaction is obviously attractive but, since streaking is never observed in the diffraction pattern, it is probably much smaller than the NN repulsion normal to the rows. (3) The best value for the heat of adsorption for O on W(110) is $\lesssim 126$ kcal/mole, from flash-desorption experiments,[7] but the interpretation of this number in terms of A-S binding energy is unclear because of lateral interactions and the possibility of oxide formation during the flash.

The apparatus used for this work consisted of a LEED diffractometer with a movable Faraday-cup detector that allows measurement of both the intensity and the angular width of diffracted beams. The system response function was measured by measuring diffracted-beam widths from a well-prepared clean W surface for different electron energies and different sized detectors and is approximately Gaussian with wings slightly above Gaussian. The measured coherence width for the electron energies and the 1-mm-diam aperture used in these experiments is $\simeq 100$ Å. The W crystal was prepared and cleaned in ultrahigh vacuum in the standard manner.[8] The $p(2\times1)$ layer was formed in several different ways,[9] all of which gave reproducible LEED intensities, indicating that the measurements reported here were made from a surface with maximum coverage and order in the $p(2\times 1)$ structure. Superlattice-beam angular profiles at room temperature were instrument limited, indicating adsorbate coherent domains of greater than 100 Å width.

The presence of an order-disorder transition for this system can be seen by observing the temperature dependence of the diffracted beams, shown in Fig. 1. The slope of $\ln I$ versus T, through the Debye-Waller factor, is of course related to the vibrational amplitude of surface atoms. The sudden departure from linearity for the superlattice reflections indicates an order-disorder transition. An order-order transition is excluded by the absence of any new superlattice beams above the transition.

Information on the nature of the new sites occupied after the disordering can be obtained by observing the intensity of the (00) beam for the O-covered surface. If the O binding site changes, the intensity profile I versus E above the transition should be different and the $\ln I$-versus-T plot should depart from linearity at those energies at which the oxygen makes a large contribution to the total scattering. Neither of these were observed; hence the transition involves only a single type of O binding site. The previously empty rows in the overlayer are becoming randomly populated, a situation analogous to substitutional disorder in binary alloys, the A and B sublattices in the ordered state being occupied respectively by O atoms and vacancies.

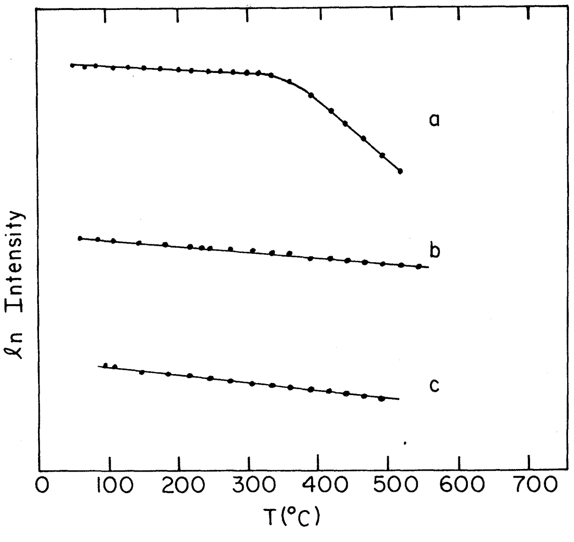

FIG. 1. Temperature dependence of LEED reflections: curve a, superlattice reflection showing order-disorder transition, $(\frac{1}{2}\frac{1}{2})$ beam, 24 eV, $\theta = 6°$; curve b, clean substrate, (00) beam, 54 eV, $\theta = 6°$; curve c, O-covered substrate, (00) beam, 132 eV, $\theta = 7°$.

In order to determine whether long-range correlations are preserved, the superlattice-beam widths were measured. If long-range order is preserved, the beam intensities decrease with increasing short-range disorder, but the beam widths remain unchanged, as for example in Bragg-Williams disorder.[10] For the ordered O layer on W(110), superlattice-beam angular widths increase with temperature during disordering as is demonstrated in Fig. 2. For comparison, the width of a beam for the clean surface is also shown. Its width is due to instrumental broadening (equal to that produced by an ordered region of ≃ 100 Å in diameter) and is thus as narrow as any beam will ever appear in the diffractometer. The presence of sharp superlattice reflections says only that ≃ 100-Å-diam ordered islands are present at room temperature. The picture of the disordering then is one of islands that decrease in size with increasing temperature, the atoms hopping out of close-packed rows into equivalent vacant sites. Long-range correlations are not necessarily preserved in overlayers, as has been implicitly assumed.[11,12]

In order to make quantitative comparison with our measurements, we have calculated, using a short-range-order model,[13] the diffracted intensity for kinematic scattering from a chain of atoms. The use of a kinematic calculation is jus-

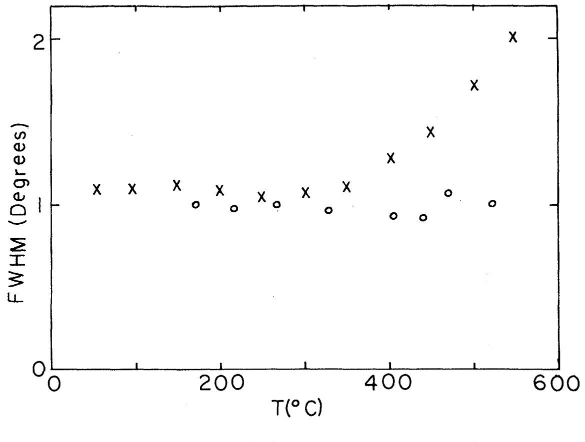

FIG. 2. Dependence of the angular width of diffracted beams on temperature. $E = 89$ eV, angle of incidence $\theta = 7°$. Circles, clean substrate, (00) beam; crosses, $(\frac{1}{2}\frac{3}{2})$ superlattice reflection.

tified because the intensity is calculated at fixed diffraction variables and energy, as a function only of overlayer order.[14] The assumed one-dimensional interaction is used as a first approximation to describe the disordering into the empty rows, and is justified if the interaction along the filled rows is weaker than that normal to them.

The diffracted intensity can be written[13]

$$I(\vec{S}_{\parallel}) = \tfrac{1}{4} N |f_{\rm O}|^2 \times \textstyle\sum_n [1 - 2P_{AB}(\vec{r}_n)] \exp(i\vec{S}_{\parallel} \cdot \vec{r}_n), \qquad (1)$$

where $\vec{S}_{\parallel}$ is the momentum transfer parallel to the surface, N is the number of sites in the layer, and $f_{\rm O}$ is the effective O scattering factor. The sum includes all different surface vectors $\vec{r}_n$. $P_{AB}(\vec{r}_n)$ is the autocorrelation function of the overlayer structure, i.e., the probability of finding an oxygen-vacancy pair separated by the vector $\vec{r}_n$. The overlayer order thus enters through $P_{AB}(\vec{r}_n)$, which yields the order parameters

$$\alpha_n = 1 - 2P_{AB}(\vec{r}_n). \qquad (2)$$

The problem reduces to determining α_n.

To compare with experiment, the instrument response, $T(\vec{S}_{\parallel})$, must be considered.[15] The measured intensity is given by

$$J(\vec{S}_{\parallel}) = I(\vec{S}_{\parallel}) * T(\vec{S}_{\parallel}). \qquad (3)$$

Combining Eqs. (1)-(3) and using the convolution theorem gives

$$J(\vec{S}_{\parallel}) = \tfrac{1}{4} N |f_{\rm O}|^2 \textstyle\sum_n t(\vec{r}_n) \alpha_n \exp(i\vec{S}_{\parallel} \cdot \vec{r}_n), \qquad (4)$$

where $t(\vec{r}_n)$ is called the transfer function. $T(\vec{S}_{\parallel})$ is experimentally accessible as already described.

Considering only a repulsive NN interaction, all α_n are expressible in terms of a single parameter p, the probability of having unlike nearest neighbors along the chain. The order parameters then are[10]

$$\alpha_n = (1 - 2p)^n. \qquad (5)$$

If this model is adequate, both the change in the intensity and the change in angular width of the superlattice reflections with temperature should give the same value for p. Figure 3 shows to what extent this is true. The filled circles give the measured decay of the relative intensity as a function of temperature. The dashed curve represents the intensity obtained by matching the widths of the superlattice beams (crosses in Fig. 2) and using the values of p thus obtained to calculate the intensities. The comparison is reasonable in view of the simplicity of the model; however, it is clear that the inclusion of NNN interactions, necessary for island growth as discussed earlier, will improve the match.

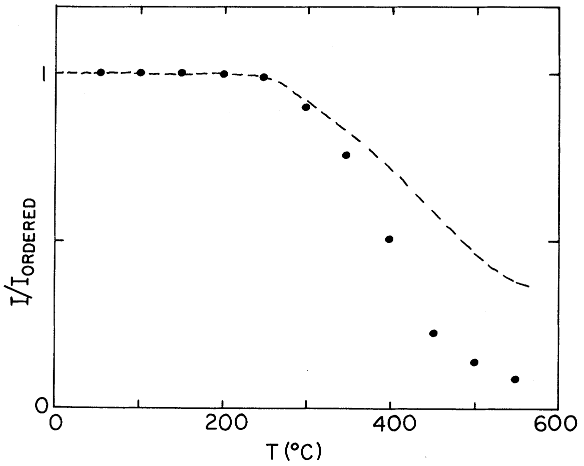

FIG. 3. Dependence of reduced intensity on temperature. $I_{\rm ordered}$ is obtained by extending the linear portion of ln$I$ versus T. Filled circles are the experimental values from Fig. 1. Dashed line is the intensity calculated from the crosses in Fig. 2.

Mindful of the limits of this model, the values of p versus T can be used to calculate the NN repulsive-interaction energy. Under the assumption that the population of sites is determined by Boltzmann statistics, the enthalpy difference ΔH between the ordered and random configurations is given by[16]

$$(1 - p)/p \propto \exp(-\Delta H/kT). \qquad (6)$$

Plotting $\ln[(1-p)/p]$ versus $1/T$ with use of the limiting values of p obtained by matching the experimental angular widths and intensities yields straight lines with slopes corresponding to $\Delta H = 0.43$ and 0.68 eV/atom.

In summary, the $p(2\times1)$-O structure is seen to disorder substitutionally, with ordered islands shrinking in size. To our knowledge, this is the first systematic measurement of the angular width of diffracted beams for an overlayer order-disorder transition. The islands are >100 Å in diameter at room temperature but are only on the order of 10 Å in diameter at 600°C. By use of a short-range-order model to describe the disordering, order parameters are obtained and the lateral-interaction energy determined directly by comparison to experiment. Including NN repulsive interactions only gives an enthalpy difference

0.43 eV/atom $\leq \Delta H \leq 0.68$ eV/atom between the ordered and disordered states at half-monolayer coverage. This number is, as expected,[12] about 10% of typical A-S binding energies. The uncertainty in the value could probably be reduced by including NNN interactions. Although the measurements were made for half-monolayer coverage, the nature of the disordering of the islands suggests that this lateral-interaction energy should be the same at much lower coverages. Experiments are in progress to check this.

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X-Ray-Diffuse-Scattering Evidence for a Phase Transition in Tetrathiafulvalene Tetracyanoquinodimethane (TTF-TCNQ) *

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X-ray-diffuse-scattering measurements of tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ) show structural evidence of a phase transition. The low-temperature three dimensional superlattice $(2a \times 3.7b \times Xc)$ is found to be preceded above 40 K by one-dimensional fluctuations or a one-dimensional distortion visible up to 55 K.

Earlier studies of the dc, microwave, and optical properties have shown that tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) is not a simple metal.[1-9] Above 58 K, there is an energy gap[6] at $\hbar\omega_g = 0.14$ eV and an extremely narrow conductivity mode centered at zero frequency. Near 58 K, TTF-TCNQ undergoes a metal-insulator transition[1,10] to a high-dielectric-constant[3] semiconductor in which the oscillator strength is shifted from zero frequency and pinned in the far infrared.[6]

In an earlier work,[1] it was proposed that above 58 K, the electrical transport in this compound is dominated by superconducting fluctuations associated with a Peierls instability in which a phonon mode is driven soft by the one-dimensional (1D)