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Dynamics of Two-Dimensional Ordering: Oxygen Chemisorbed on the W(112) Surface

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Low-energy electron diffraction has been used to study the dynamics of formation of oxygen $p(2\times 1)$ superlattice structure on a W(112) surface at a half-monolayer coverage. The ground state of the $p(2\times 1)$ structure is twofold degenerate and the nonconserved long-range order associated with this structure was found to grow linearly with time in the earlier stages. This behavior is interpreted with use of the domain-growth theory proposed by Lifshitz and by Allen and Cahn. The temperature dependence of the growth rate obeyed an Arrhenius law for $T/T_c \leqslant 0.4$.

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Chemisorbed overlayers frequently form ordered superstructures at low temperatures and a disordered lattice gas at higher temperatures. This order-disorder transition is described quantitatively by a nonconserved long-range order parameter which vanishes for $T \geqslant T_c$ but remains finite for $T < T_c$, where T_c is the critical temperature.

Recently, the dynamical evolution of order in an overlayer from an initially disordered state has been a subject of considerable practical[1] and theoretical[2-6] interest. The basic theory for the time evolution of the nonconserved, order-disorder transition has been developed by Lifshitz[7] and by Allen and Cahn[8] (LAC). This theory assumes that after the system is quenched from a disordered to an ordered state, domains separated by antiphase boundaries are formed. The long-range order parameter of the individual domains is close to the equilibrium value. These domains will then grow to reduce the curvature of the boundaries. The theory predicts that the domain size grows as a function of time as $t^{1/2}$. This growth law has been observed experimentally in various three-dimensional alloys.[8] The same growth law was predicted[3,7] for two-dimensional systems with the number of ground-state degeneracies $p < 3$. For $p \geqslant 3$, a much slower growth law was proposed. Theoretical studies of the dynamical evolution of overlayer ordering with nonsaturated coverage,[4] and of the Q-state Potts model,[6] have also been carried out with use of Monte Carlo simulation.

In this Letter, we report a low-energy electron diffraction (LEED) study of the dynamical evolution of the $p(2\times 1)$ superstructure of oxygen chemisorbed on a W(112) surface. The structure of a clean surface[9] is shown in Fig. 1. The perfection of the surface has been characterized by angular profile analysis of LEED beams, and the defectfree regions were found to be > 200 Å. Also shown in Fig. 1 are the two unit meshes for the two possible $p(2\times 1)$ oxygen antiphase domains ($p = 2$) that may exist at room temperature.[9]

Figure 2 shows the experimentally determined temperature versus coverage phase diagram (T-θ) of the W(112)$p(2\times 1)$-O system for $0 < \theta < 1$. Each data point, representing a transition temperature at a fixed coverage, was obtained from the inflection point of the intensity versus temperature curve of the half-order beams measured by LEED. The data points form a second-order

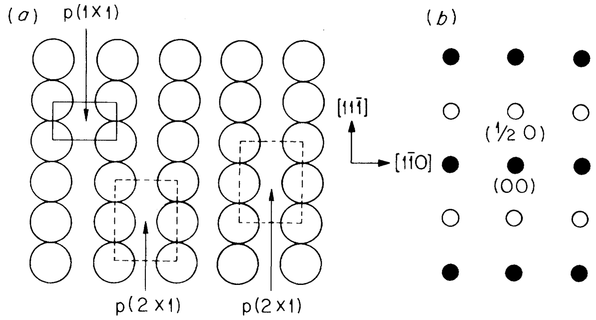

FIG. 1. (a) Schematic drawing of a W(112) surface. Open rectangle: (1×1) unit mesh of the clean surface. Dashed rectangles: two possible antiphase positions of the $p(2\times 1)$ unit mesh of the oxygen overlayer. (b) Schematic LEED W(112)$p(2\times 1)$-O pattern at half a monolayer. Filled circles: integral-order beams. Open circles: half-order beams.

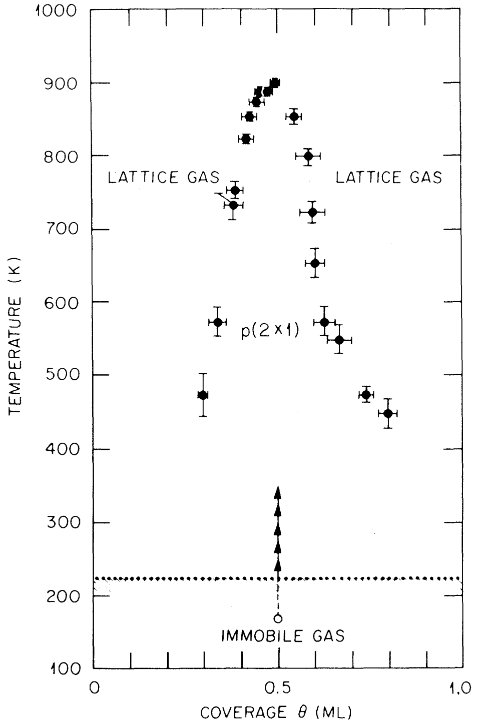

FIG. 2. Phase diagram of the W(112)$p(2\times1)$-O overlayer. The open circle indicates the initial oxygen adsorption temperature which is below the immobile boundary (dotted line). The arrows indicate the various final up-quenching temperatures into the $p(2\times1)$ ordered regions.

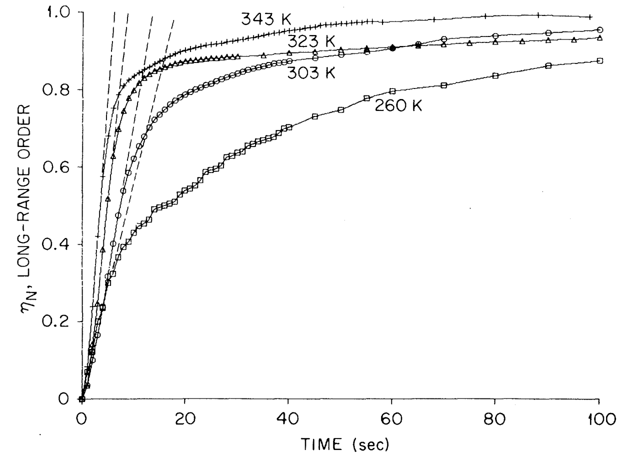

FIG. 3. Time dependence of the long-range order parameter for various up-quenching temperatures. Dashed lines represent the linear time dependence of the order parameter predicted by Lifshitz and by Allen and Cahn.

phase boundary which separates the low-temperature $p(2\times1)$ phase and the high-temperature lattice-gas phase. The oxygen overlayer is not mobile for $T < 225$ K, the region under the dotted line.

For half a monolayer coverage, this system undergoes a second-order order-disorder phase transition at $T_c = 899$ K.[10] According to the classification scheme suggested by Domany *et al.*, this transition belongs to the Ising universality class.[11] The order parameter has only one component and the ground state is twofold degenerate.

In the study of dynamic evolution, the adsorption of 0.5±0.05 monolayer oxygen took place at a crystal temperature $T_0 = 170$ K in a UHV chamber (8×10^{-11} Torr). At this temperature, electron diffraction showed no superlattice beams and the oxygen overlayer was a two-dimensional immobile gas giving only a diffuse background intensity. We then "up quenched" the crystal from $T_0 = 170$ K to an elevated temperature T (as shown by the arrows in Fig. 2) by radiation heating from the back side of the crystal. The up-quenching technique has been used to study the formation of the ordered structure of oxygen chemisorbed on a W(110) surface.[12] The temperature was measured by W26%Re-W5%Re thermocouple wires attached to the crystal surface. For quenching temperature $T > 260$ K, superlattice diffraction beams developed. The beams first appeared to be faint and broad and then became brighter and sharper with time. The peak intensity of the diffracted superlattice beam was measured by a Faraday cup with an aperture which admits a 1.5° acceptance angle with respect to the sample.

The $(\frac{1}{2}0)$ superlattice beam intensities were measured as a function of time. Figure 3 is a plot of the normalized long-range order parameter η_N, which is the square root of the normalized intensity, as a function of time for different up-quenching temperatures T. η_N has been normalized to the final (long but finite time) value[13] of the long-range order parameter. Time zero ($t = 0$) is the time when the half-order beam intensity began to increase above the background intensity. Heating was started within three seconds prior to $t = 0$. The final temperature was reached less than one second after $t = 0$ for all cases.

According to the LAC theory, the size of the domains should grow after quenching as $t^{1/2}$. The domain area, which is proportional to the long-range order parameter, should grow linearly with time. The dashed lines in Fig. 3 are therefore the prediction of the theory. This growth law is seen to describe the time dependence of the

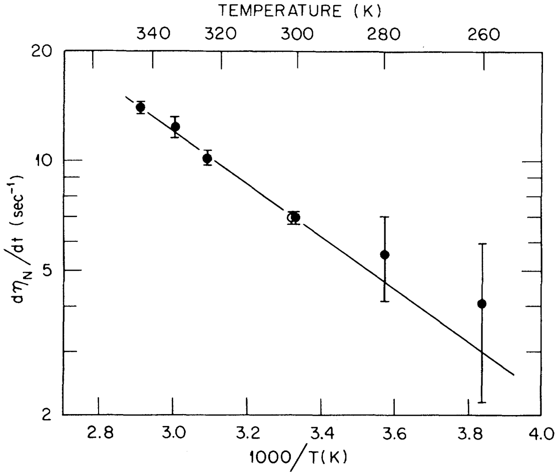

FIG. 4. Growth rate of the long-range order parameter as a function of inverse temperature.

order parameter quite well for initial domains which do not approach their ultimate extent too closely. We have not yet been able to describe quantitatively the experimental data over the entire range of time.

The growth rate of the order parameter, $d\eta_N/dt$, is temperature dependent. In Fig. 4, we plot $\log(d\eta_N/dt)$ as a function of $1/T$ for the temperature ranging from $T/T_c = 0.29$ to 0.38. This linear behavior indicates that, for the range of temperature under consideration, the growth rate is of Arrhenius type, i.e.,

$$d\eta_N/dt \propto \exp(-\alpha/kT),$$

where α is the activation energy for atomic migration, the value of which can be obtained from the slope of the line in Fig. 4; it is equal to 0.14 ± 0.02 eV.

Recently, Sahni *et al.*,[6] have shown by a Monte Carlo simulation that α itself may be strongly temperature dependent for $T/T_c \geq 0.6$. They suggested that the deviation of α from a constant value is due to thermal fluctuations. Unfortunately, because of the rapid change of the intensity for temperatures $T/T_c \geq 0.4$, we were not able to measure the initial increases in intensity accurately.

In summary, we show that the two-dimensional dynamical evolution of the oxygen $p(2\times1)$ structure on a W(112) surface obeys Lifshitz-Allen-Cahn domain-growth theory and that the growth rate can be described by an Arrehenius law for $T/T_c \leq 0.4$.

This method of combining LEED techniques with quenching (up or down) may be applicable to the studies of the dynamics of other adsorbate systems, the reconstructed domain growth of clean surfaces, and the epitaxial growth of crystals.

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