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Dynamical scaling in the domain growth of a chemisorbed overlayer: W(112)(2×1)-O

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We observed a self-similar growth (scaling of oxygen antiphase domains) of the (2×1) structure chemisorbed on the W(112) surface using time-resolved, high-resolution, low-energy electron diffraction technique. The initial stage of domain growth after the system was quenched from a lattice-gas state was shown to obey a curvature-driven mechanism. The scaling function was extracted from the angular distribution of the intensity of the $(\frac{1}{2}\,0)$ beam and was compared with recent analytical theories and Monte Carlo simulations. Breakdown of scaling was observed after the termination of the curvature-driven regime.

The dynamical evolution of a two-dimensional (2D) system, such as a chemisorbed overlayer, quenched from a disordered state far from equilibrium to an ordered state has recently attracted intense interest.[1–14] These studies have been focused on important physical concepts such as universality, conservation laws, growth exponent, and scaling. These concepts are tested through the study, either theoretically or experimentally, of the evolution of order domains generated from the disordered state. It has been found[2] that the growth dynamics can be grouped into a small number of classes which depend only on the dimensionality and symmetry of the system, but not on the detailed microscopic interactions among the constituents that give rise to the collective phenomena.

The simplest type of growth process is perhaps the system with a twofold degenerate ground state (DGS) and a nonconserved order parameter. It is well known that the evolution of the ordered domains at the initial stage obeys the Lifshitz-Allen-Cahn (LAC) growth law;[1] i.e., the time-dependent average domain size $\bar{R}$ follows $\bar{R} \propto t^{1/2}$, where t is the time. This growth law can be derived from an interface curvature-driven mechanism. Recent Monte Carlo simulations[2–6] and experiments[11–13] have confirmed the existence of this growth process in two dimensions. Monte Carlo simulations[3–6] and theories[7–10] predict a self-similar growth in the early time regime in which the structure factor contains a time invariant scaling function $F(x)$:

$$S(\mathbf{k},t)=\bar{R}^{2}(t)F(x)\ , \tag{1}$$

where $\mathbf{k}$ is the momentum transfer vector parallel to the surface and $x=k/\bar{k}$ and $\bar{k}$ is inversely proportional to the characteristic length $\bar{R}$. In this paper we report the first 2D scaling measurement of the LAC type of domain growth in a 2D Ising overlayer using a newly developed high-resolution low-energy electron diffraction (HRLEED) technique[15] and compare the scaling function $F(x)$ extracted from the data with the existing theories and Monte Carlo simulations. To our knowledge the only reported experimental work that observed the 2D scaling behavior was by Tringides *et al.*[14] on a chemisorbed system which has a fourfold DGS and has distinctly different growth kinetics.

The system we chose was oxygen chemisorbed on a clean W(112) surface at 0.5 monolayer (ML) coverage. The oxygen overlayer forms a (2×1) superstructure which has a twofold DGS. This overlayer undergoes a 2D Ising-like order-disorder phase transition at ~900 K.[16] During the phase transition the order parameter is not conserved. It has been previously shown[12] that the growth of (2×1) domains follows LAC growth kinetics, i.e., $\bar{R} \propto t^{1/2}$, during the early state of ordering after the system was quenched from a disordered state.

The experiment was performed in an UHV chamber equipped with a HRLEED and a cylindrical mirror Auger analyzer. The base pressure was $6.5-8\times10^{-11}$ Torr. The preparation and cleaning of the W(112) surface, the sample mounting, as well as the temperature measurement, have been described elsewhere.[16] The terrace width of the clean W(112) surface was estimated from the half-order beam profiles (using a Gaussian distribution) to be about 410±10 Å and 115±5 Å along the $[11\bar{1}]$ and $[1\bar{1}0]$ directions, respectively. A typical 0.5-ML oxygen coverage requires 0.4 langmuir (1 L $=10^{-6}$ torr sec) exposure with an oxygen partial pressure of $\sim1\times10^{-9}$ torr. The determination of the 0.5-ML oxygen coverage was described elsewhere.[17] The oxygen atoms were absorbed at ~350 K after a flash cleaning of the W(112) substrate at ~2430 K. At this adsorption temperature a random 2D lattice gas was formed.[16–18] The sample was subsequently up quenched and held at a temperature T where oxygen atoms were mobile. The time required for the up quenching to a predetermined temperature was typically less than a few seconds. While the (2×1) domains were growing, the angular distribution (profile) of the $(\frac{1}{2}\,0)$ superlattice beam intensity, which is a measure of the structure factor $S(\mathbf{k},t)$, was measured as a function of time. Depending on the up-quenching temperature, the entire LAC growth period could be as long as $10^{2}-10^{3}$ sec from the time of quench.

Figure 1 shows the development of the peak intensity of the $(\frac{1}{2}\,0)$ beam versus time from the 0.5-ML (2×1)-oxygen overlayer at different up-quenching temperatures.

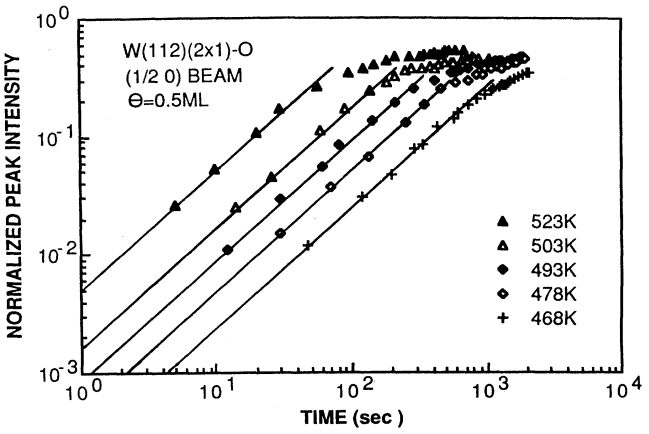

FIG. 1. The time-dependent peak intensity of the $(\frac{1}{2}0)$ beam diffracted from W(112)(2×1)-O overlayer at 0.5 ML coverage is plotted for different up-quenching temperatures. Each curve was normalized to the maximum intensity from a well-annealed overlayer. The incident electron energy is 55 eV. The solid lines represent the power-law fit in which the slope was found to be 1.01±0.02.

A very weak peak intensity I_0 at $t=0$ just after the quench has been subtracted from the time-dependent peak intensity $I(t)$ in Fig. 1.[18] From Fig. 1 we see that on a log-log scale the peak intensity grows linearly with time in the early stage and then levels off. The peak intensity I_p is a measure of the mean-squared domain size,[3–6,19] i.e., $I_p \propto \bar{R}^2$. Assuming a power growth law $\bar{R}^2 \propto t^n$ in the early stage, the exponent n extracted from the slope of the log-log plot in Fig. 1 was found to be 1.01±0.02, which is independent of up-quenching temperature. This result remarkably demonstrates the LAC growth law that has been reported previously.[12]

In this study of scaling we have measured the angular profiles in both the $[1\bar{1}0]$ and $[11\bar{1}]$ directions at different evolving times. A low uniform background intensity ($\lesssim 4\%$ of the peak intensity) near $t=0$ was observed in the measured angular profile. As the peak intensity was developing, the ratio of the background intensity to the peak intensity became smaller and eventually approached zero. This low background intensity has been subtracted from the measured angular profiles. All the profiles presented here have been deconvoluted with an effective instrument response function which has a narrow width ($\sim 0.012\pm0.002$ Å^{-1}).[20] The deconvoluted profiles reflect the true structure factor $S(\mathbf{k},t)$. Considering $\bar{R}^2 \propto I_p$ and taking $\bar{k}$ as the full width at half maximum (FWHM) of the angular profile, we obtained the measured scaling function $F(x)=S(\mathbf{k},t)/I_p$. This equation implies that if the normalized angular profiles at different evolving times are plotted in the $x=k/\bar{k}$ coordinate (not in the k coordinate), i.e., scaled by its own FWHM, then all the profiles should superpose on each other. It is known that the shape of the angular distribution of intensity reflects domain size distribution. Scaling law implies that, although the average domain size increases with time, the functional form of the size distribution does not change. Figures 2(a) and 2(b) are the plots of the scaling functions $F_1(x)$ and $F_2(x)$ for various times in both $[1\bar{1}0]$ and $[11\bar{1}]$ directions, respectively. The up-quenching temperature was 493 K. As seen from these figures, within the LAC growth regime (<240 sec, see Fig. 1), the profiles scale very well in both directions. Even more remarkable is that $F_1(x)$ and $F_2(x)$ almost coincide with each other as shown in Fig. 3, despite the fact that the average domain sizes in these two directions at any given time were different (before the scaling, i.e., in the k coordinate, the FWHM of a profile in the $[1\bar{1}0]$ direction is at least two times wider than that in the $[11\bar{1}]$ direction at the same time). Similar agreement was obtained for other up-quenching temperatures. Furthermore, the scaling profiles obtained at different up-quenching temperatures

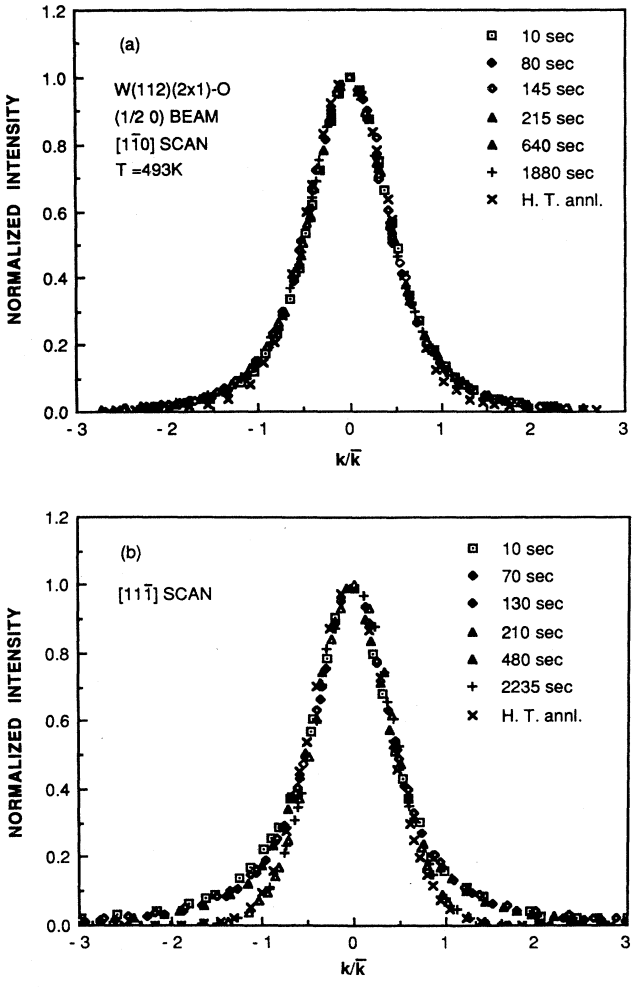

FIG. 2. The scaled angular profiles of the $(\frac{1}{2}0)$ beam for various times at $T=493$ K are plotted according to Eq. (1). (a) Scans along the $[1\bar{1}0]$ direction. (b) Scans along the $[11\bar{1}]$ direction. The scaling holds only for $t<240$ sec where the power-law growth applies. The H.T. annl. means a profile obtained after the overlayer has annealed to ~ 670 K. The vertical error bar is less than twice the size of the symbol due to the statistical fluctuations of intensity in the initial times.

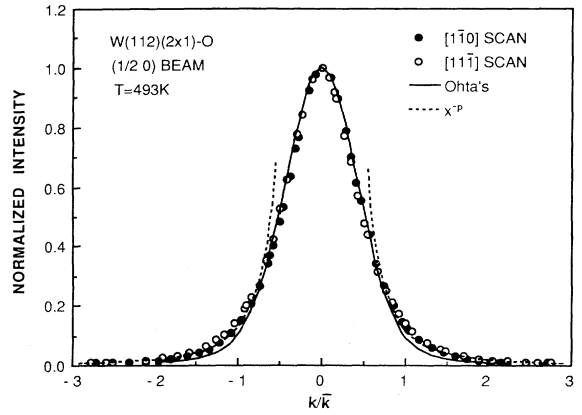

FIG. 3. Typical scaled angular profiles from Fig. 2 are presented. Solid circles (●): a scan along the [1$\bar{1}$0] direction at $t=215$ sec. Open circles (○): a scan along the [11$\bar{1}$] direction at $t=210$ sec. The solid curve represents a fit of the theory predicted by Ohta *et al.* (Ref. 8). The dashed curve represents the fit of x^{-p} with $p=2.9\pm0.1$ in the limit of $|x|\geq 1.0$.

are identical, too. Therefore, $F_1(x)=F_2(x)=F(x)$ is a universal function independent of direction and up-quenching temperature despite the fact that the detailed microscopic interactions among the oxygen atoms in the [1$\bar{1}$0] and [11$\bar{1}$] directions are not isotropic.[16,21,22]

The scaling behavior in the kinetics of domain growth has been a subject of a variety of theoretical discussions.[7–10] For the system with a twofold DGS, Kawasaki *et al.*[7] first described scaling of the correlation function by considering the time-dependent Ginzburg-Landau model in a weak-coupling, long-time limit. Ohta *et al.*,[8] using the LAC interface curvature-driven model, have derived an approximate, but explicit expression for the scaling function $F(x)$. They predicted that the 2D scaling function has the form

$$F'(x')=\frac{4}{x'}\int_0^\infty d\mu\,\mu^2[\exp(\mu^2)-1]^{-1/2}J_1(\mu x') , \qquad (2)$$

where J_1 is the Bessel function of the first kind and $x'=k\bar{R}(t)$ with $\bar{R}(t)\propto t^{1/2}$. In the derivation of Ohta *et al.* they have assumed the system is isotropic and has randomly distributed smooth interfaces with a Gaussian correlation. In order to fit Eq. (2) with the experimental data shown in Fig. 3, one needs to adjust the unknown proportionality constant c between x' and x, i.e., $x'=cx$. Equation (2) can be manipulated and rewritten in a series form which is more convenient for numerical evaluation:

$$F(x)=4\sum_{k=0}^{\infty}(-1)^k\frac{(cx)^{2k}}{2^k k!}\times\left[1+\frac{1}{2}\left[\frac{1}{3}\right]^{k+2}+\frac{(1)(3)}{(2)(4)}\left[\frac{1}{5}\right]^{k+2}+\frac{(1)(3)(5)}{(2)(4)(6)}\left[\frac{1}{7}\right]^{k+2}+\cdots\right], \qquad (3)$$

where the variable $x=k/\bar{k}$ of the function $F(x)=F'(x')$ is now directly related to the horizontal scale in Fig. 3 through $x'=cx$ with the proportionality constant c as the fitting parameter. The best-fitted profile is plotted as the solid curve in Fig. 3. The fitting shows good agreement with experiment in the small $|x|$ (<1.0) regime but deviates somewhat in the tails. In the plot, the calculated profile has been normalized using $F(0)=2\pi\ln 2\approx 4.355$.[8] The proportionality constant c was found to be ~ 2.34 in the [1$\bar{1}$0] direction and ~ 2.30 in the [11$\bar{1}$] direction. The fitting in the [11$\bar{1}$] direction has the same behavior as that in the [1$\bar{1}$0] direction but was not presented in Fig. 3.

The theory predicted by Kawasaki *et al.*[7] has essentially the same scaling behavior as that of Ohta *et al.*, although they were based on different approaches. Subsequently, Mazenko and Valls[9] calculated the scaling function based on the renormalization-group method combined with Monte Carlo simulations. Their prediction for the scaling function of this system with a nonconserved order parameter is rather similar to that of Ohta *et al.* except for the intermediate values of the scaling variable, i.e., the tail of the scaling function calculated from the renormalization-group theory is higher than that of Ohta *et al.* Therefore the measured scaling function in Fig. 3 may be in better agreement with the results of Mazenko and Valls.[9] However, Ref. 9 provided an analytical expression only for a limited range of x and we cannot use it to fit the entire measured scaling function. All these theories exhibit a Gaussian behavior in the small-x regime and a Porod's law[23] behavior in the large-x regime. That is, for large x,

$$F(x)\approx x^{-p} , \qquad (4)$$

where $p=d+1=3$ (d is dimensionality). Ohta *et al.*[8] obtained $p=3$ from Eq. (2) and Mazenko and Valls obtained $p=3.1$.[9] These values of p are also within the uncertainty of Monte Carlo simulations by Sahni *et al.*[3] ($p=2.9$) and by Kaski *et al.*[4] ($p=2.7$) given in Ref. 9. We have also fitted the tail part ($|x|\geq 1.0$) of our scaling profiles using Eq. (4) and found $p=2.9\pm0.1$. This is done by ignoring the data for $|x|<1.0$. As seen in Fig. 3, the fitting is very good for $|x|\geq 1.0$, which indicates that the dimensional dependence of the exponent p in Eq. (4) is consistent with the theories, including the Monte Carlo simulations.

Recently, by considering the statistical properties of randomly distributed smooth and isotropic interfaces with a Gaussian correlation (originally considered by Ohta *et al.*[8]), Tomita[10] has obtained an asymptotic expression for the structure factor which gives a leading correction to Porod's law. This correction term was also included in the theory of Ohta *et al.*, but Tomita, using a different method, assigned a physical meaning to this term which is related to the interface area density and average curvature of the domains. Using the scaling function derived from Tomita's formula to fit our scaling profiles at $|x|\geq 1.0$, we found that the fitting is almost as good as the previous fit with $p=2.9\pm0.1$. The contribution of the correction term is small ($\sim 0.5\%$). We have also fitted the entire measured scaling profile $F(x)$ by a Gaussian function and the result is far worse.

The angular profile of the $(\frac{1}{2}0)$ beam was also measured beyond the LAC growth regime [>240 sec, see Figs. 2(a) and 2(b)]. For the profiles scanned along the $[1\bar{1}0]$ direction, scaling still holds for $t>240$ sec, but there is small deviation when the sample was annealed to a higher temperature (670 K) to accelerate the growth process. The data are shown in Fig. 2(a). An apparent breakdown of scaling was observed in the $[11\bar{1}]$ direction for $t>240$ sec, as shown in Fig. 2(b). Furthermore, the function $F(x)$ in the $[11\bar{1}]$ direction behaves quite similarly for $t\gtrsim 480$ sec as compared to that of the well-annealed profile. After the annealing the domains approached their ultimate sizes which were limited by the surface heterogeneity of the substrate. The breakdown of scaling is an indication of the termination of the curvature-driven process. One possible origin of the observed termination of the curvature-driven process might be due to the finite-size effect. At the point that the peak intensity levels off ($t\simeq 240$ sec for $T=493$ K), the domain size has already grown to $0.51R_1$ and $0.70R_2$, where R_1 and R_2 are the average terrace width in the $[1\bar{1}0]$ and $[11\bar{1}]$ directions, respectively. Previous Monte Carlo simulations[24] have estimated that finite-size effects become important when $\bar{R}\simeq 0.4R_f$, where R_f is the finite area used in the simulations. We estimated that the average domain sizes were $\sim 0.51R_1$ and $0.60R_1$ in the $[1\bar{1}0]$ direction, and $0.70R_2$ and $0.91R_2$ in the $[11\bar{1}]$ direction for $t\sim 240$ and 2230 sec, respectively. In the $[1\bar{1}0]$ direction, the growth was very slow after $t\sim 240$ sec, and therefore the profile did not change too much. In the $[11\bar{1}]$ direction considerable growth was observed after $t\sim 240$ sec. The distribution of domain sizes changed into the size distribution defined by the terrace width, and as a result, the function $F(x)$ changed shape. This finite-size effect may explain why we did not observe a clear crossover to a later stage where the growth rate slows down. We must point out that even for an ideal surface where the growth is not limited by finite size and a later growth regime may exist, there is no reason to believe that the function $F(x)$ obtained in the later stage should scale the same way as that in the LAC growth regime. It would therefore be desirable to have a surface with a larger average terrace width so that the behavior of the function $F(x)$ in the unconstrained later stage of growth can be studied unambiguously.

In summary, the self-similar scaling in the (2×1) domain growth of oxygen overlayer on the W(112) surface at 0.5 ML coverage was observed by the analysis of time-resolved HRLEED angular profiles of the $(\frac{1}{2}0)$ beam. The scaling function extracted from the angular profiles was found to be a universal function independent of the growth direction and the up-quenching temperature, and was compared with recent analytical theories and Monte Carlo simulations. An obvious breakdown of scaling in the $[11\bar{1}]$ direction was observed after the peak intensity levels off. This was attributed to the finite-size effect dictated by the surface heterogeneity.

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[18]To be precise, for the pure oxygen overlayer case, a very weak intensity I_0 [1.6% of the peak intensity obtained from the well-annealed (2×1)-O overlayer] was recorded at the $(\frac{1}{2}0)$ beam position at $t=0$ just after the quench. This indicates that many very small (2×1) domains have been formed at $t=0$. In fact, the configuration which contains many small domains is a necessary condition for the initiation of the curvature driving growth, see, for example, Ref. 1. This intensity I_0 has been subtracted out in the determination of the domain

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