

## Growth Kinetics of a Chemisorbed Overlayer in the Presence of Impurities

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The effects of random impurities on the growth kinetics of oxygen chemisorbed on the W(112) surface at half-monolayer coverage are studied by high-resolution LEED. An apparent deviation of the Lifshitz-Allen-Cahn growth law of the  $(2\times 1)$  domains is observed in the presence of nitrogen impurities in the early stage after the mixed overlayer is quenched from a random-lattice-gas state. An effective power law for the domain growth with  $\bar{R}^2 \sim t^x$ , where  $\bar{R}$  is the average size of the domain, can be established. The effective exponent  $x$  is found to decrease from 1 as the density of the impurity increased. This result is consistent with recent theoretical calculations based on a random-field Ising model.

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In this Letter we report a high-resolution low-energy electron-diffraction study of the effects of random impurities on the equilibrium and growth kinetics of the oxygen overlayer chemisorbed on a clean W(112) surface at half-monolayer (ML) coverage. We found that the long-range order was destroyed with a small amount of predosed random nitrogen impurity. We have discussed and interpreted our data on the basis of the theoretical random-field Ising model which was originally proposed by Imry and Ma<sup>1</sup> and has attracted great attention both theoretically<sup>2</sup> and experimentally<sup>3,4</sup> since then. We also observed a clear deviation from the classic Lifshitz-Allen-Cahn linear-domain growth law after the mixed overlayer was quenched from a random lattice-gas state. Recently, there has been much discussion<sup>5-10</sup> on the issues involving the dynamics of the random-field Ising model. Our present work represents the first experimental study of the dynamical behavior of this model.

Oxygen chemisorbed on a W(112) surface forms a  $(2\times 1)$  superlattice structure over a wide range of submonolayer coverages.<sup>11</sup> The system has twofold ground-state degeneracy. At half-monolayer coverage, the system undergoes a two-dimensional (2D) Ising-type order-disorder phase transition at  $\approx 900$  K.<sup>12</sup> The dynamics of the  $(2\times 1)$  domain growth was also studied with use of an "up-quenched" technique.<sup>13,14</sup> In this technique, oxygen was adsorbed on the surface at low temperature in a form of random lattice gas (immobile) and the system was then quenched up to an elevated temperature to form ordered  $(2\times 1)$  domains. The same technique was used in the present experiment.

The experiment was performed in an ultrahigh-vacuum chamber with a base pressure of  $(6.5-8)\times 10^{-11}$  Torr. The angular distribution of the diffracted intensity was measured with a high-resolution low-energy electron diffractometer,<sup>15,16</sup> which is capable of resolving domain size of the  $(2\times 1)$  structure from a few angstroms to 2000 Å. (A conventional LEED diffractometer can resolve domain size only up to  $\approx 200$  Å.) The terrace width of the clean W(112) surface was estimated to be

at least  $\approx 300$  Å by detailed analysis of the (00) beam as a function of the incident electron beam energy.<sup>17</sup> Both the predosed nitrogen and the oxygen were adsorbed at  $\approx 350$  K where a random 2D lattice was formed.<sup>11,18</sup> The coverage was determined by our monitoring the  $(\frac{1}{2}0)$ -beam peak intensity as a function of the exposure after the overlayer was fully annealed. The 0.5-ML coverage was obtained when the peak intensity reached its maximum value and the full width at half-maximum (FWHM) was the narrowest.<sup>11,12</sup> This procedure of determining the 0.5-ML coverage of oxygen was also applied to the N predosed case. The N dose ranged from 1 langmuir (1 L =  $10^{-6}$  Torr sec) to 10 L which corresponds to coverage of 0.5% to 5% ML. The N coverage was determined by Auger-electron spectroscopy, except for coverage less than 1% ML which was obtained by an extrapolation procedure. The Auger-electron spectroscopy result on coverage determination is also in agreement with a previous thermal desorption result.<sup>19</sup>

The angular profiles of the  $(\frac{1}{2}0)$  beam for the well-annealed sample were observed to broaden considerably (accompanied by a reduction of the peak intensity) in the case of N-contaminated O layers as shown in Fig. 1. The profiles were measured in the  $[1\bar{1}0]$  direction. Similar behavior was found for profiles measured in the  $[11\bar{1}]$  direction. The incident electron energy used in this experiment was 55 eV. The broadening of the angular profiles indicated that the  $(2\times 1)$  domain size in the mixed overlayer did not reach the same size as in the pure O-overlayer case which was limited only by the surface heterogeneity. This result can be interpreted as an evidence of the destruction of the overlayer long-range order by random N impurities. A similar broadening effect has been observed in the neutron-diffraction angular profile of a diluted antiferromagnet in a uniform field.<sup>3,4</sup> The nitrogen impurities are believed to adsorb on the surface randomly. This conclusion is based on the fact that the FWHM of the well-annealed mixed overlayer is always broader than the FWHM of the well-annealed pure oxygen overlayer at *all* oxygen coverage.<sup>20</sup>

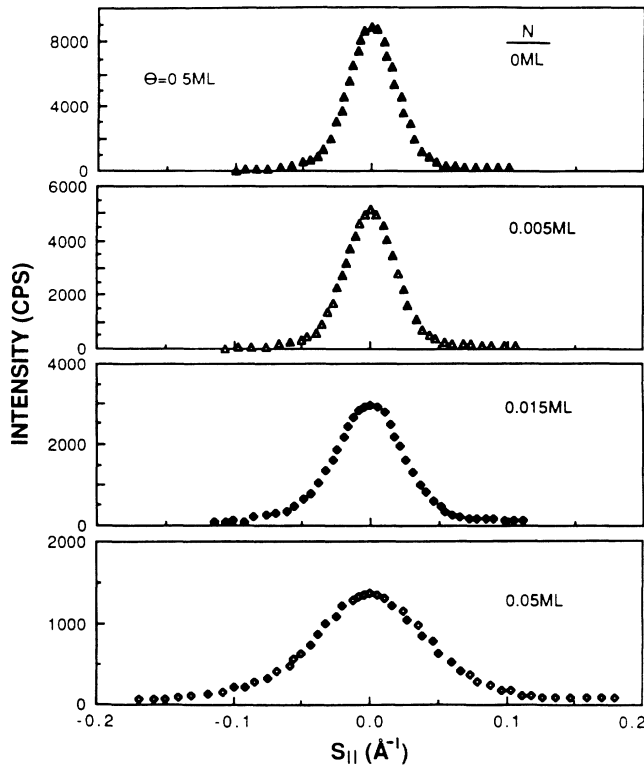


FIG. 1. The high-resolution LEED angular profiles of the well-annealed  $(\frac{1}{2}0)$  beam diffracted from the  $W(112)(2 \times 1)$ -N + O mixed overlayers at half-monolayer coverage are plotted for various N content. The profiles were measured at  $T=320$  K, and the incident electron energy was 55 eV. CPS means counts per second.

Also, the degree of broadening increases as the amount of preadsorbed nitrogen is increased. If a fixed, but small, amount of preadsorbed nitrogen clustered on the surface, then the FWHM obtained from the mixed O + N overlayer, especially for the low-O-coverage ( $<0.4$  ML) case, should not broaden as compared with the FWHM obtained from the pure O overlayer. The impurities may create static random fields<sup>9,21</sup> and disturb the periodic surface potential to give local minima of the free energy which obscure the equilibrium state of the overlayer. The broadening of the  $(\frac{1}{2}0)$ -beam angular profiles and the large reduction of the peak intensity are the results of the diffraction from finite-size domains which are stabilized by the presence of the random N atoms and are separated by antiphase boundaries. The system is then a 2D physical realization of the well-known random-field Ising model which has a lower critical dimension of 2, and has been a subject of intense discussions recently.<sup>1-4</sup>

A stronger support for the above interpretation of the random-field effects comes from the observation of the dramatic alteration of the domain growth kinetics from the simple Lifshitz<sup>22</sup> and Allen and Cahn<sup>23</sup> (LAC) growth law for the O + N mixed overlayer.

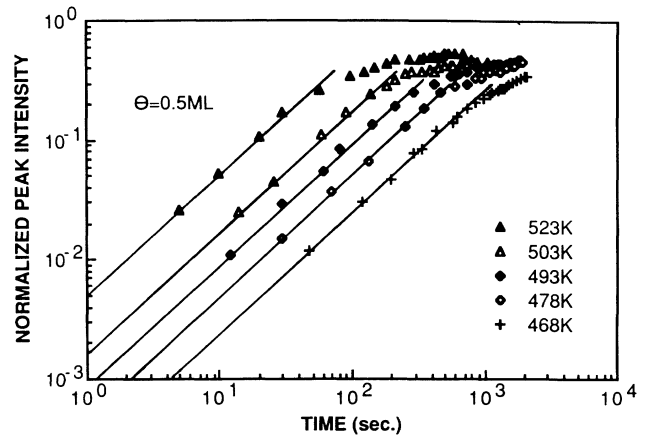


FIG. 2. The time dependence of the normalized peak intensity (with respect to the well-annealed intensity) of the  $(\frac{1}{2}0)$  beam diffracted from the  $W(112)(2 \times 1)$ -O overlayer (without N impurity) at half-monolayer coverage is plotted for different up-quenching temperatures ranging from 468 to 523 K in the zero-field case (no preadsorbed N). The peak intensity is a measure of the square of the domain size,  $\bar{R}^2$ .<sup>24</sup> The slopes were measured to be very close to 1 ( $1.01 \pm 0.02$ ) at the initial linear growth regime and were independent of the temperature. This is a remarkable demonstration of the LAC curvature-driven kinetics.<sup>22,23,25,26</sup> From Fig. 2, there is deviation from the LAC growth behavior at the later stage of growth. At the present time there is no good theoretical understanding of this late stage of growth.<sup>25</sup>

Shown in Fig. 2 are log-log plots of the peak intensity normalized to the well-annealed intensity of the  $(\frac{1}{2}0)$  beam as functions of the growth time for different up-quenching temperatures ranging from 468 to 523 K in the zero-field case (no preadsorbed N). The peak intensity is a measure of the square of the domain size,  $\bar{R}^2$ .<sup>24</sup> The slopes were measured to be very close to 1 ( $1.01 \pm 0.02$ ) at the initial linear growth regime and were independent of the temperature. This is a remarkable demonstration of the LAC curvature-driven kinetics.<sup>22,23,25,26</sup> From Fig. 2, there is deviation from the LAC growth behavior at the later stage of growth. At the present time there is no good theoretical understanding of this late stage of growth.<sup>25</sup>

We must also note that the LAC theory only applies to systems which have twofold degenerate ground states. Recent theoretical<sup>26</sup> and experimental<sup>14</sup> results on O/W(110) system, which has a ground-state degeneracy of 4, showed that even for the pure oxygen overlayer case, the domain growth did not obey the LAC law. Growth kinetics that do not follow the LAC theory were also observed in other 2D systems.<sup>27-29</sup>

A dramatic change of the growth kinetics was observed when the system was preadsorbed with N impurity as shown in Fig. 3. These curves were obtained for different N coverages at a fixed up-quenching temperature of 493 K. Following the suggestion of previous computer simulations,<sup>9,30</sup> we were able to define an effective exponent  $x$  for the power growth law,  $\bar{R}^2 \sim t^x$ , from the data and deduced that  $x$  is  $\approx 0.88$ ,  $0.76$ , and  $0.70$  for N concentrations of  $\approx 0.005$ ,  $0.025$ , and  $0.05$  ML, respectively. These exponents again do not depend on the up-quenching temperature. One is then able to estimate the

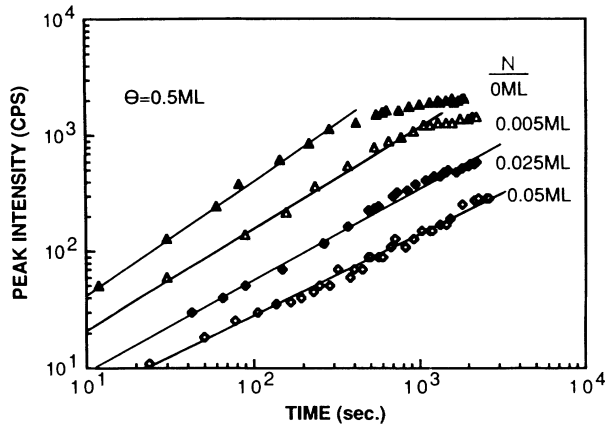


FIG. 3. The time dependence of the  $(\frac{1}{2} 0)$  beam peak intensity diffracted from the  $W(112)(2 \times 1)-(N+O)$  mixed overlayers at half-monolayer coverage is plotted for different N content at the same up-quenching temperature of 493 K. The solid lines represent the effective power-law fit. The slope changes as a function of N content and an apparent deviation from the Lifshitz-Allen-Cahn growth law is observed.

value of the random-field strength  $h$  as a function of the N concentration by comparing our value of  $x$  to the results of computer simulation.<sup>9</sup> The  $h$  was found to be 0.18 to 0.48 which corresponds to the N concentration of 0.5% to 5% ML; a summary of the results is given in Table I. The random field we used so far was thus small.

Recently Grant and Gunton described the evolution of the curvature of a convoluted domain-wall structure in the presence of a random field and predicted that  $\bar{R}^2 \sim t[A - B(h^2 \ln t)]$ .<sup>8</sup> For small  $h$ , their theory reduces to a power-law-type behavior. Our observation is therefore consistent with their theory.

From Fig. 3, it is seen that the curves with 0- and 0.005-ML N deviate from the power law at a later stage of growth. One would be tempted to interpret this deviation as the termination of the curvature-driven mechanism.<sup>22,23</sup> The domains might have approached their local equilibrium configuration and reached their maximum size. The system then crossed over to the logarithmic

TABLE I. Result of an estimation of the random-field strength  $h$  for different N doses. The result was obtained by our comparing the value of the exponent  $x$  obtained in this experiment for different N doses with that of the computer simulation for different random-field strengths reported in Ref. 9. A relationship was thus established between the N doses and the field strength  $h$ .

N (L)	N (ML)	$x$	$h$
0	0	$1.01 \pm 0.02$	0
1	0.005	$0.88 \pm 0.02$	0.18
5	0.025	$0.76 \pm 0.02$	0.38
10	0.05	$0.70 \pm 0.02$	0.48

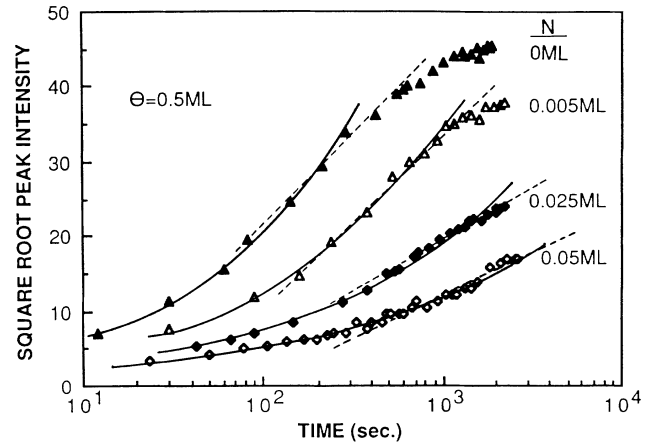


FIG. 4. The same data shown in Fig. 3 are replotted in a semilog plot. The solid curves are the effective power-law fit described in Fig. 3 and the dashed lines represent possible  $\ln t$  growth regimes.

mic growth regime proposed by Villain<sup>5</sup> and by Grinstein and Fernandez.<sup>6</sup> This later stage of growth is controlled by thermal fluctuations which roughen the domain walls during growth.

To study this effect more closely, we replotted the data, in a semilog plot, i.e.,  $\bar{R}$  (square root of the peak intensity) as a function of  $\log t$ , as shown in Fig. 4. The solid curves are the power-law fit with the exponents obtained from the linear fit shown in Fig. 3. Again, for the 0.025- and 0.05-ML cases, the data for the entire time domain are consistent with the power-law description. For 0- and 0.005-ML N cases, there is a clear deviation from the power-law behavior at the later stage of growth. The part that obviously deviated from the power law also cannot be described by a logarithmic growth law which should behave linearly. However, in each curve, the last portion of the data which can be fitted by the power law is also consistent with a logarithmic growth law as indicated by the dashed lines. (The logarithmic growth regime, if it exists, should occur before the curve starts to be concave downward.<sup>2b)</sup> We may conclude from Fig. 4 that there is definitely an initial-stage regime that can be attributed to the curvature-driven mechanism which gives rise to a power growth law for all the four curves. From our data it is not clear that the system under study has passed through a logarithmic growth regime which is associated with thermal fluctuations. This is because within the experimental uncertainty the portions of the data which can be described by a logarithmic law are also consistent with the power law.

In summary, we have used high-resolution LEED to study the effects of N impurities on the ordering kinetics of oxygen overlayer chemisorbed on the  $W(112)$  surface at half-monolayer coverage. We found the destruction of the overlayer equilibrium behavior and the deviation

of the LAC domain growth law in the presence of a small quantity of N impurities. We have interpreted and analyzed our results within the context of recent theories of the random-field Ising model.

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