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# Formation of a Metastable Ordered Surface Phase Due to Competitive Diffusion and Adsorption Kinetics: Oxygen on Pd(100)

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A metastable $c(2\times2)$ structure is formed by atomic oxygen on Pd(100) under conditions of slow diffusion *combined with rapid adsorption.* We propose that formation of the $c(2\times2)$ under these conditions must be controlled by characteristics of the dissociative adsorption event itself.

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In the past twenty years, there has been a great deal of research into the characteristics of two-dimensional phase diagrams of small molecules adsorbed on surfaces (e.g., Roelofs[1] and Woodruff, Wang, and Lu[2]). Structures formed under *nonequilibrium* conditions (metastable structures) remain uncharacterized, presumably because of expectations that they will simply exhibit a high degree of disorder, and thereby prove largely uninteresting. Indeed, conditions where surface diffusion is slow (low substrate temperature) have been used deliberately to prepare metastable disordered adlayers of oxygen for studies of temperature-dependent ordering kinetics (e.g., Thiel, Yates, Jr., and Weinberg[3] and Wang and Lu[4]). We report in this Letter that a metastable *ordered* structure can be formed by atomic oxygen on Pd(100) under extreme conditions of slow diffusion *combined with rapid adsorption.* Observations of such metastable structures is predicted to be a general phenomenon which is related directly to the nature of the adsorption step.

The experiments are carried out in a standard ultrahigh-vacuum chamber equipped with instrumentation for Auger-electron spectroscopy, low-energy electron diffraction (LEED), and quadrupole mass spectrometry. The background pressure is below $2\times10^{-10}$ Torr prior to oxygen dosing. Oxygen gas is introduced via a leak valve by backfilling the entire chamber. A detailed description of the video-LEED system used in this experiment can be found elsewhere.[5]

It is well known that oxygen adsorbs dissociatively on Pd(100) at room temperature, forming two stable ordered structures: a $p(2\times2)$ with an ideal coverage of 0.25 monolayer, and a $(\sqrt{2}\times\sqrt{2})R45°$ [also known as a $c(2\times2)$] with an ideal coverage of 0.50 monolayer.[6,7] (One monolayer, $\theta=1$, is defined here as one adsorbed particle per surface Pd atom, $1.03\times10^{15}$ particles $\mathrm{cm}^{-2}$.) The phase diagram is very similar to that of oxygen on Ni(100).[8] The forces which give rise to the $p(2\times2)$ and $c(2\times2)$ phases are believed to be mainly pairwise: strong nearest-neighbor (nn) repulsions, weak second-nn repulsions, and weak third-nn attractions.[7-9] For both Pd(100) and Ni(100), it has been reported that the adsorption probability drops close to zero at 0.25 monolayers and, because of this, exposures in excess of 50 L (1 L$\equiv10^{-6}$ Torr s) are necessary to remove all traces of the $p(2\times2)$ and and form the well-ordered $c(2\times2)$.[7,9] Our own findings corroborate these statements.[10] Furthermore, we observe that atomic oxygen can form a *metastable $c(2\times2)$ structure* under conditions of low sample temperature and high oxygen pressure. The metastable $c(2\times2)$ is formed under conditions much different from those described for the stable $c(2\times2)$, because it is not preceded by the $p(2\times2)$ phase and it forms at a relatively low exposure.

Two physical processes whose rates can be controlled during formation of an adsorbed layer are dissociative adsorption and atomic diffusion. To a first approximation, these rates vary as simple functions of two experimental parameters: gas impingement rate (gas pressure) and sample temperature, respectively. In Fig. 1 we show the development of intensity of two LEED spots as a function of oxygen exposure for various combinations of oxygen pressure and sample temperature. The $(0,\frac{1}{2})$ spot signals only the $p(2\times2)$ structure, whereas the $(\frac{1}{2},\frac{1}{2})$ spot is present both for the $p(2\times2)$ and $c(2\times2)$ lattices. Figures 1(a)-1(c) indicate the development of intensity in these features at constant (low) impingement rate and at decreasing sample temperature; Figs. 1(d)-1(f) show the same data at an impingement rate which is 2 orders of magnitude higher. In all cases, but one, the $p(2\times2)$ pattern forms first and attains its maximum intensity at 0.8-1.3-L exposures, then fades slowly as the $c(2\times2)$ pattern develops. This sequence indicates that diffusion is fast relative to adsorption, so that the stable structures can form during adsorption. Note that as sample temperature decreases the maximum intensity of the $p(2\times2)$ diminishes at both impingement rates. This trend is more marked at the higher impingement rate, as shown by Figs. 1(d)-1(f). Figure 1(f) represents the extreme in this trend: At an oxygen impingement rate on the order of $10^{14}$ $\mathrm{cm}^{-2}$ $\mathrm{s}^{-1}$ and sample temperatures of 150-180 K, the $c(2\times2)$ forms immediately and there is no evidence of an intermediate $p(2\times2)$ structure. This result is completely reproducible.

LEED *I-V* curves of the $(\frac{1}{2},\frac{1}{2})$ beam are very similar both for the $c(2\times2)$ which is formed under conditions of slow diffusion and rapid adsorption [Fig. 1(f)] and for the $c(2\times2)$ which can be formed at 300 K with exposures of several hundred langmuirs.[10] This indicates that

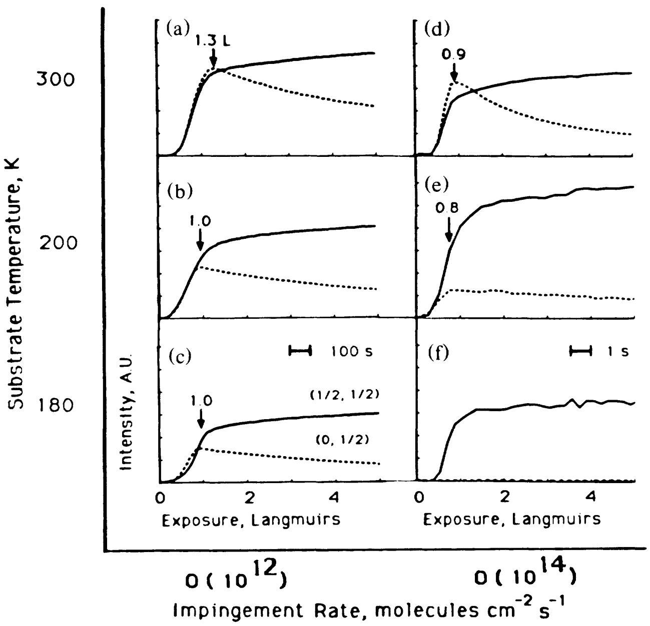

FIG. 1. Changes in intensity of $(\frac{1}{2},\frac{1}{2})$ and $(0,\frac{1}{2})$ LEED spots during adsorption of oxygen on Pd(100), normalized to an integral-order spot of the clean surface. Each of the curves [(a)–(f)] shows the results of an individual experiment, at the sample temperature and oxygen impingement rate indicated. The impingement rates on the left and right sides are $(1.1 \pm 0.1)\times 10^{12}$ and $(6\pm 3)\times 10^{13}$ $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$, respectively. Each intensity axis represents the same (arbitrary) scale.

the arrangement of atomic nuclei in the immediate vicinity of an oxygen nucleus within the $c(2\times 2)$ layer is the same in both cases, i.e., the $c(2\times 2)$ is due to atomic oxygen in the same adsorption site, no matter how it is prepared.

Following an exposure of 1 L in the experiment of Fig. 1(f), Auger-electron spectroscopy shows that the coverage of oxygen is the same as that obtained after a 1-L exposure in the other experiments: $0.25\pm 0.03$ monolayer.[10] At this coverage, the $c(2\times 2)$ prepared under the conditions of Fig. 1(f) can be annealed to 300 K without measurable change in oxygen coverage. A $p(2\times 2)$ pattern develops during the annealing. Figure 2 shows the quantitative variation in LEED spot intensity and spot width during the annealing process. The $(\frac{1}{2},\frac{1}{2})$ spot represents a sum of intensity contributions from the oxygen $c(2\times 2)$ and $p(2\times 2)$ patterns. Therefore, the $I(T)$ function for the $c(2\times 2)$ pattern has been obtained by subtracting $I(T)$ of the $(0,\frac{1}{2})$ beam, multiplied by an empirically determined factor of 1.4, from $I(T)$ of the $(\frac{1}{2},\frac{1}{2})$ spot. The result, shown in Fig. 2(a), clearly shows that annealing causes *loss* of $c(2\times 2)$ regions and simultaneous *gain* of $p(2\times 2)$ domains. This is irreversible. Therefore, the $c(2\times 2)$ formed at low temperature and at high impingement rates is a *metastable* (kinetically frozen) structure which reverts to the $p(2\times 2)$ when diffusion "turns on." The $c(2\times 2)\longrightarrow p(2\times 2)$ transformation appears to take place in two distinct stages. This will be discussed more fully elsewhere.[10] The variation in spot profile widths, shown in Fig. 2(b), indicates that the $c(2\times 2)$ islands are initially quite small (30 Å diam), whereas the ultimate $p(2\times 2)$ island size is circa 150 Å.[2]

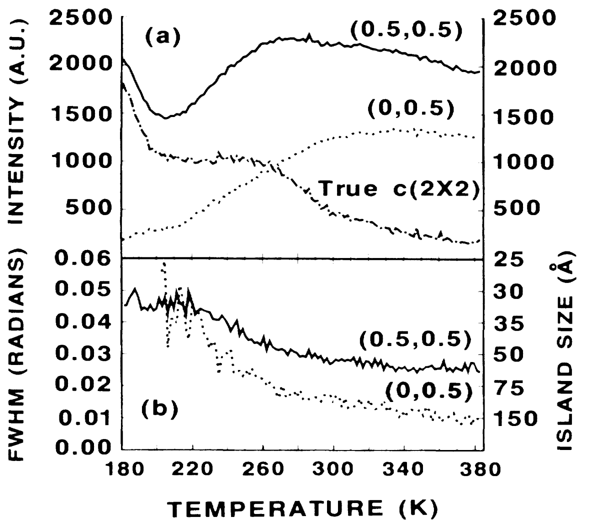

FIG. 2. (a) Variations in integrated LEED spot intensities during annealing from 180 to 380 K in vacuum, following adsorption as shown in Fig. 1(f). The curve representing the "true $c(2\times 2)$" intensity has been obtained as described in the text. The heating rate is 1 K/s. All data are taken *at* the indicated temperature, with no correction for Debye-Waller attenuation of intensity. (b) Variations in full width at half maxima (FWHM) of LEED spots. The island sizes shown on the right abscissa are derived from the FWHM by assuming the islands have a constant, circular diameter, as described in Ref. 2. The analysis of the $(\frac{1}{2},\frac{1}{2})$ spot is based on the assumption that it represents entirely $c(2\times 2)$ islands (which is only true at $T<200$ K), whereas the $(0,\frac{1}{2})$ spot represents only $p(2\times 2)$ islands at all values of $T$. The difference in values for the island size at any given temperature derived from these two curves is due primarily to the difference in lattice constants $a$ for the two structures: $a=3.89$ Å for the $c(2\times 2)$ structure and $a=5.50$ Å for the $p(2\times 2)$ structure.

Molecular, chemisorbed oxygen has been identified as a stable species on Pd(100) at temperatures below 120 K.[11] In order to preclude its influence in our experiments, we use coadsorption of oxygen isotopes ($^{18}O_2$ and $^{16}O_2$) to identify a thermal desorption feature at 150 K as the molecular state, based on the lack of isotopic scrambling within this feature. Assuming first-order desorption kinetics and $\nu=10^{13}\ \mathrm{s}^{-1}$, the molecular state has a binding energy of 9 kcal/mol.[12] Our adsorption experiments are performed at temperatures $\geq 180$ K and oxygen pressures $\leq 10^{-7}$ Torr. The values of the desorption kinetic parameters can be used to calculate that the *maximum* equilibrium coverage of molecular oxygen is $10^{-4}$ monolayer under these conditions. In short, the molecular chemisorbed state is not significantly populated during adsorption in our experiments.

We have also investigated aspects of the adsorption kinetics using Auger-electron spectroscopy and thermal desorption spectroscopy. The initial adsorption probability, $S_0$, at 150 K appears to be close to unity and is roughly twice that at 300 K, which suggests the existence of an intrinsic precursor to dissociative chemisorption. This precursor is most probably chemisorbed molecular oxygen, which is observed directly at lower temperature.[11] Assuming that this is true, the lifetime of the intrinsic precursor is on the order of $10^{-2}$ s or less in the experiments of Fig. 1. This can be compared with the time between adsorption events at or near a single surface site, which is on the order of $10^3/S_0$ s at an impingement rate of $10^{12}$ cm$^{-2}$ s$^{-1}$ [Figs. 1(a)-1(c)], or $10^1/S_0$ s at an impingement rate of $10^{14}$ cm$^{-2}$ s$^{-1}$ [Figs. 1(d)-1(f)]. Given that $S_0$ is on the order of 1, it is clear that the lifetime of the intrinsic precursor is far too short to be influenced by the variation of impingement rate in the regime described by the experiments of Fig. 1. Therefore, the intrinsic precursor cannot play a significant role in the suppression of $p(2\times2)$ and formation of $c(2\times2)$ at high impingement rates and low sample temperatures.

At higher coverages, $S(\theta)$ decreases. The saturation coverage decreases as temperature increases: The saturation coverage at 150 K is only circa 0.35 monolayer. We propose the following general model: When diffusion is *fast* relative to adsorption [as in Figs. 1(a)-1(e)], stable structures can form sequentially during adsorption; however, when diffusion is *slow* relative to adsorption [as in Fig. 1(f)], small metastable islands of $c(2\times2)$ form coexistent with low-density regions of disorder and domain boundaries. The time scale of diffusion which is necessary for $p(2\times2)$ formation can be quantified by considering that if the time between impingement events at a single site is less than $10^1$ s, diffusion is too slow to allow $p(2\times2)$ formation [Fig. 1(f)], but when this time is on the order of $10^3$ s, diffusion is sufficiently rapid that $p(2\times2)$ formation can take place [Fig. 1(c)]. If the necessary diffusion lifetime ($\tau$) then is on the order of $10^2$ s at $T=180$ K, and assuming a preexponential factor in the diffusion rate constant ($\nu$) of $10^{13}$ s$^{-1}$, we can calculate the activation barrier for diffusion ($E_a$) from

$$E_a = kT\ln(\nu\tau) = 12.5 \pm 1 \text{ kcal/mol}.$$

This number compares favorably with activation barriers for oxygen diffusion measured on Ir(111),[13] Rh(111),[14] and W(112).[4]

The formation of the metastable $c(2\times2)$ islands under conditions of rapid adsorption and slow diffusion must result from some characteristic of the adsorption event itself. We can envision two ways in which this might occur.

In 1984, Brundle, Behm, and Barker proposed that an empty eight-site ensemble is necessary for dissociative adsorption of one oxygen molecule on Ni(100), on the basis of Monte Carlo simulations of the coverage dependence of the adsorption probability at 300 K.[15] This ensemble, enclosed by the shaded rectangle in Fig. 3, may also be necessary for dissociative adsorption of oxygen on Pd(100). Let us first assume that the oxygen atoms are at thermal equilibrium with the metal surface immediately following dissociation. If adsorption is rapid relative to diffusion, then some molecules may adsorb randomly into adjacent, overlapping ensembles in such a way that small domains of $c(2\times2)$ are created immediately upon adsorption. Because adsorption is fast, they become locked into these $c(2\times2)$ clusters before they can respond to the weak second- and third-nn forces by hopping away. Meanwhile, other molecules adsorb randomly into ensembles which are not of the correct phase to continue the $c(2\times2)$ overlayer, and which trap empty space between domain boundaries. Figure 3 illustrates this effect. A recent Monte Carlo simulation by Evans[16] indicates that rather large domains of $c(2\times2)$ are created under these conditions.

The second case in which a $c(2\times2)$ might form under nonequilibrium conditions is one in which the oxygen atoms *do not* equilibrate immediately following dissociation. Rupture of the oxygen-oxygen bond and formation of the Pd—O chemisorption bond is (net) exothermic by 0.8 eV per atom.[10] Depending upon the efficiency of energy transfer to the surface, it may be that the oxygen atoms carry excess translational kinetic energy for some distance before finally coming to equilibrium with the cold metal. Note that such transient motion is not a "normal" type of surface diffusion. The result could be

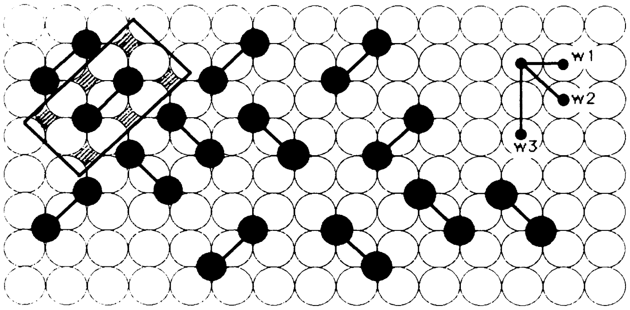

FIG. 3. Illustration of random, immobile dimer adsorption into the empty eight-site ensembles described by Brundle, Behm, and Barker (Ref. 15). The products of each dimer's dissociation are connected by straight lines, but this only reflects the bond of the *original* molecule, and does not imply that a bond remains after dissociative adsorption. The open circles represent Pd atoms in the (100) plane, and the filled circles represent oxygen atoms. The pairwise forces between the oxygen atoms are shown as w1 (strong first-nn repulsion), w2 (weak second-nn repulsion), and w3 (weak third-nn attraction) (Refs. 7–9).

to make the translationally hot atoms unresponsive to the weak second- and third-nn interactions, leaving only the strong first-nn repulsions in effect while the atoms move and lose energy to the metal. The filling of the Pd(100) lattice would then bear some similarity to random, immobile filling of a square lattice with only nn exclusions operating between single particles.[17] Such a process would again generate small islands of the $c(2\times2)$ phase in coexistence with trapped empty spaces between antiphase domains, as shown in Fig. 3.

At this point we cannot determine which (if either) of these two models is correct. Certainly more complex models could be envisioned.[16] The main point is that our data indicate that metastable ordered structures may be generally observed under conditions where the adsorption rate dominates the diffusion rate. A systematic survey of these structures could yield unique information about the dynamics of the adsorption process and may prove useful as a tool in preparing kinetically frozen ordered phases of small molecules on surfaces.

In summary we find that a metastable ordered structure can be formed by atomic oxygen on Pd(100) under conditions of rapid adsorption and slow diffusion. We propose that formation of the $c(2\times2)$ must be controlled by the characteristics of the dissociative adsorption event itself, and we advance two possible models to explain our results. In these models, $c(2\times2)$ formation is linked to the adsorption step either by the ensemble of sites necessary for dissociative adsorption of a single molecule or else by transient motion which takes place as the atoms equilibriate with the metal after dissociation of the molecule.

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