Knowledge about chemisorption overlayer structures and their thermodynamic behavior at high coverages provides the bases for a molecular level understanding of relevant surface processes occurring under normal atmospheric pressure conditions. On thermodynamical grounds, the common phenomenon of domain wall structure formation in chemisorption systems, especially at high adsorbate coverages, represents a compromise between a chemisorption bonding interaction and inter-adsorbate repulsion. Indeed, the chemisorption system of CO on metal surfaces has received by far the most attention over the years, which is reflected in the large body of literature [1,2], including detailed Monte Carlo simulations based on semi-quantitative CO adsorption potential energy surfaces. Conclusions drawn from such theoretical modelling of CO are anticipated to be applicable to other simple adsorbates as well [2]. A closely related adsorbate molecule is NO, since chemisorbed NO has similar binding energies as CO on most transition metal surfaces and both molecules have similar electronic structures. On noble metals such as Pt and Pd, the adsorption of NO is predominantly molecular in nature [3]. Despite its important role as a prototypical molecule in surface science studies aimed at controlling NO emission in auto exhaust, relatively little is known about the nature of dense chemisorbed NO layers in general.

In this Letter, we report the observation of ordered phase/antiphase domain formation of adsorbed NO on Pd(111) at high coverages ($>0.5$ monolayers, ML, or $\theta > 0.5$) and the development of adsorbate structural models based upon LEED and infrared spectroscopy.

The experiments were carried out in a combined UHV/high-pressure system described elsewhere [4]. A Mattson Fourier transform infrared spectrometer (Cygnus 100) equipped with a liquid nitrogen cooled HgCdTe detector was used to record the vibrational spectrum in a single reflection mode at an instrumental resolution of $4 \text{ cm}^{-1}$. The Pd(111) crystal (10 mm diameter disk) could be resistively heated to $\sim 1300 \text{ K}$ and cooled to $\sim 90 \text{ K}$ by liquid nitrogen. Initial sample cleaning involved cycles of Ar$^+$ bombardment followed by annealing at 1200 K. After the initial cleaning steps, a clean Pd(111) surface could be routinely produced by annealing at 850 K in $\text{O}_2$ ($\sim 10^{-6} \text{ Torr}$) to remove trace amounts of carbon, followed by a flash to 1200 K. LEED patterns were photographed from the phosphor screen in a reverse view geometry. To minimize electron beam effects on the NO overlayer, precaution was taken to avoid prolonged beam expo-
Fig. 1. LEED patterns formed by NO adsorption on Pd(111) (a) (2 × 2) at 105 eV and 120 K; (b) (8 × 2) at 200 K; (c)–(e) transition structures at 230, 235 and 240 K; (f) c(4 × 2) at 242 K. The electron energy for (b)–(f) was 73 eV. (g) Schematic single domain pattern of the 8 × 2; (h) single domain pattern of the c(4 × 2). Note only half of the c(4 × 2) spots are split to give the 8 × 2.
sure on a single spot on the crystal. The electron gun was only switched on during the time period necessary for the LEED photography.

Two ordered NO structures on Pd(111) have been reported in previous LEED studies conducted under UHV conditions [5,6]. In agreement with these studies, a well-ordered c(4 × 2) LEED pattern was used to define a half monolayer (θ = 0.5) coverage of NO. At saturation NO exposure, the Pd(111) surface exhibited a 2 × 2 LEED pattern. To facilitate the formation of a truly equilibrium ground state configuration of adsorbed NO at θ > 0.5, the Pd(111) surface was first slowly cooled (~ 0.5 K/s) to a particular temperature under a typical equilibrium NO pressure of ~ 1 × 10⁻⁶ Torr in the high pressure chamber. Then, the system was slowly evacuated to UHV for IR measurements and/or translated to the UHV section for LEED analysis. Following such a procedure, a new LEED pattern, designated here as “8 × 2”, was observed upon cooling to 220 ± 5 K (fig. 1b). This LEED pattern contained a characteristic splitting of the 1/2-order diffraction spots. Reducing the NO coverage by slowly annealing the 8 × 2 overlayer in UHV produced streaks at the 1/2-order position (figs. 1c–1f); the structure eventually converted to the more familiar c(4 × 2) at ~ 240 K.

In order to acquire further information about the types of adsorption sites involved, reflection IR measurements were carried out in conjunction with the LEED studies. The complete details of the IR study will be reported in a separate publication [7]. Fig. 2 shows selected IR spectra of the NO overlayer corresponding to the LEED conditions in fig. 1. The NO saturation-coverage spectrum exhibits a stretching frequency at 1758 cm⁻¹ and is readily identified as NO adsorbed at atop sites by analogy to nitrosyl data [8]. However, based on nitrosyl data alone, the band at 1586–1620 cm⁻¹ falls midway between atop (1650–2000 cm⁻¹) and two-fold bridge (1480–1545 cm⁻¹) NO and, in fact, coincides with the frequency range of bent on-top NO. This has often been the case for adsorbed NO on a number of metal surfaces [10–16], and has created difficulties and some ambiguities in assigning NO adsorption sites when an independent structural determination is lacking. Nevertheless, existing surface vibrational studies generally have integrated bands in this frequency range arising from NO at two-fold bridge sites, assigned using LEED data and/or surface symmetry arguments. Such examples include a 1585 cm⁻¹ band on Ni(111) [16]; a 1581 cm⁻¹ band on Rh(100) [12]; a 1610 cm⁻¹ band on Pt(110) [13]; a 1675 cm⁻¹ band on Ni(110) [14] and a 1650 cm⁻¹ band on Pd(110) [15]. More recently, based on independent structural investigations [17–19], the 1585 cm⁻¹ band of NO on Ni(111), originally assigned to two-fold bridge sites [16], has been found to correspond to NO on three-fold sites! This discovery highlights a dramatic failure of adsorbate site assignment based on correlating adsorbate vibrational frequencies with that of coordination compounds. It is clear that the site assignment NO is rather complex.
Based on the above assignment, $\theta = 0.5$, corresponding to the $c(4 \times 2)$ LEED pattern, adsorption occurs exclusively onto two-fold bridge sites ($\sim 1620 \text{ cm}^{-1}$). As the NO coverage is increased, a high frequency absorption peak appears at $\sim 1734 \text{ cm}^{-1}$ indicative of atop NO sites. The trend toward atop site occupation at the expense of bridge NO species continues with increasing coverage until saturation is reached, at which point the surface adopts a $2 \times 2$ periodicity with nearly exclusive atop NO. To ensure that saturation is reached under equilibrium adsorption conditions, it is necessary to quench the Pd surface temperature under an equilibrium NO pressure so that the IR absorption peak exhibits a nearly symmetrical profile and the smallest FWHM [7]. Such an overlayer always exhibits a sharp $2 \times 2$ LEED pattern with a minimal diffuse background.

Based on the above structural and spectroscopic information, the following real space structural models of ordered NO overlayer on Pd(111) are proposed. The $2 \times 2$ and $c(4 \times 2)$ structures reflect occupation of a single type of high symmetry adsorption sites, i.e., the atop and two-fold bridge, respectively. Following the notation introduced by Biberian and Van Hove [1], the two structures can be conveniently expressed as $c(2\sqrt{3} \times 2)\text{rect}$ and $c(\sqrt{3} \times 2)\text{rect}$, respectively (figs. 3a and 3c). The $2 \times 2$ structure proposed here differs from that of a previous UHV study [6] in which case the model was based upon the observation of a substantial presence of bridging NO at saturation. We believe this discrepancy is due to the non-equilibrium nature of the low temperature UHV adsorption process. A similar situation was found for a saturation CO coverage on Pd(111) [20].

The more interesting adsorbate structure obviously lies in the coverage regime between the two limits. Taking into account the splitting of the $1/2$-order spots observed in the $8 \times 2$ LEED pattern and also the requirement of filling both atop and two-fold bridge adsorption sites, a phase/antiphase domain model is constructed as shown in fig. 3b. In this model, ordered strip domains consisting of one unit of the $c(\sqrt{3} \times 2)\text{rect}$ NO are separated by high density NO and coordination compound group frequencies should be used with great caution and then only as a guide. As to the NO/Pd(111) system, a previous HREELS study [6] found no evidence to support a bent on-top configuration. Based on our data, i.e., the persistence and dominance of this band over a very wide NO coverage range, and the ordered $c(4 \times 2)$ LEED pattern associated with this species, a two-fold bridge assignment to the 1586–1620 cm$^{-1}$ band is favored over a bent on-top or three-fold assignment. Nevertheless, in view of the recent new findings concerning the NO/Ni(111) system [17–19], further structural investigations are warranted.
Fig. 3. Structural model of the adsorbed NO: (a) $(2 \times 2)$ or $c(2\sqrt{3} \times 2)\text{rect}$ at $\theta = 0.75$; (b) "$8 \times 2$" or $c(4\sqrt{3} \times 2)\text{rect}$ at $\theta = 0.625$. The NO overlayer is drawn in unrelaxed configuration with the primitive surface unit cell indicated by dashed lines. The possible directions for NO relaxation at domain walls are indicated by small arrows for atop NO. In addition, the two-fold bridge NO may also relax toward three-fold hollow sites away from the domain walls; (c) $c(4 \times 2)$ or $c(\sqrt{3} \times 2)\text{rect}$ at $\theta = 0.5$.

domain walls running along the [1\overline{1}0] direction. This structure ($c(4\sqrt{3} \times 2)\text{rect}$) contains 2/5 bridge and 3/5 atop NO and gives rise to a NO coverage of $\theta = 0.625$. The antiphase relationship between adjacent domains only exists in one direction. Therefore only half of the 1/2-order LEED spots are split as schematically shown in fig. 1g. Compared to a few alternative domain structures possessing the same $8 \times 2$ periodicity, this structure is consistent with the bridge/atop intensity ratio observed in IR [21] and is in good agreement with kinematic LEED intensity calculations [22].

So far, the structural model only emphasizes the occupation of high symmetry adsorption sites by NO. Since physically the formation of such a domain structure represents a compromise between adsorbate–substrate bonding and adsorbate–adsorbate repulsion, the latter interaction will manifest itself in the form of relaxation of NO molecules located at the high density domain walls. This relaxation channel is made energetically favorable in the present model because, in general, the adsorption potential well associated with the parallel frustrated translational mode at an atop site is expected to have a flatter bottom compared to that at a bridge site, as has been well established for CO on Pt(111) [23]. Thus most certainly the relaxation will displace NO away from the high symmetry atop position due to unbalanced NO–NO repulsion, resulting in a “tilted” NO species as indicated schematically in fig. 3b. Evidence of such a relaxed NO structure is provided by inspecting the fine structure in the IR spectrum corresponding to the $8 \times 2$ LEED pattern (fig. 3). Since the NO at high symmetry atop site exhibits the highest N–O stretching frequency, any displacement away from this site will result in a lower N–O stretching frequency. The low frequency shoulder at $-1736 \text{ cm}^{-1}$ (fig. 2) most likely represents a contribution of N–O stretching from these displaced NO molecules. In addition to the displaced atop NO, the structural model proposed here also includes unperturbed high symmetry atop NO molecules in the low density domain regions. Together this accounts for the presence of two frequencies in the terminal N–O stretching region. Although in the model there are twice as many NO in a displaced configuration, due to vibrational coupling at such a high adsorbate coverage, substantial intensity transfer is expected to shift the intensity in favor of the high frequency branch for the two closely spaced ($\sim 10 \text{ cm}^{-1}$) IR absorption bands. In addition to the atop relaxation channel, the present system
differs from the CO/Pt(111) and CO/Pd(111) systems in that the NO relaxation at domain walls may also involve displacement of NO at two-fold bridge sites (along the [112] direction) toward three-fold hollow sites due to the unique orientation of the domain walls and expected low activation barrier. However, experimental evidence regarding this relaxation channel is less compelling. Taking this effect into account, the structural model we propose here is consistent with both the LEED and vibrational IR data.

We note that for the well-studied CO/Pt(111) system, with the construction of a semi-quantitative adsorption potential energy surface, Monte Carlo simulations [2,24] have been able to predict ordered domain superstructures at \( \theta > 0.5 \) and to reveal the precise underlining physics regarding the presence of displaced or tilted CO in these structures. This has been nicely complemented by direct experimental confirmation of tilted CO species from electron stimulated desorption ion angular-distribution (ESDIAD) measurements by Kiskinova et al. [25]. The present system NO/Pd(111) appears to be a suitable candidate for further investigation using these techniques [26], which should enable a more direct measure and better understanding regarding the details of NO orientation.

The sharp 1/8-order LEED spots observed between 110-220 K indicate the domain walls are rather straight and evenly distributed. The stability of domain walls at this rather high temperature \( (k_B T \sim 20 \text{ meV}) \) suggests a strong interaction between the walls separated by \( 2\sqrt{3} \) Pd lattice units. However, the \( (\sqrt{3} \times 2) \) rect domain unit at \( \theta = 0.625 \) is not compatible with the \( (\sqrt{3} \times 2) \) rect unit at \( \theta = 0.5 \) in terms of the types of adsorption sites involved. This precludes the low density domains from simply expanding upon decreasing NO coverage from \( \theta = 0.625 \) toward 0.5. Rather a gradual shift toward full bridge occupation must occur, as evidenced from IR data. This is also the main reason why only the \( (4\sqrt{3} \times 2) \) rect structure, but not the series of such ordered domain structures, i.e. \( (m\sqrt{3} \times 2) \) rect \( (m = 6, 8, \ldots) \), was observed between \( \theta = 0.625-0.5 \). From the direction of streaking observed in LEED, it seems that the periodicity of two Pd lattice units was preserved in the direction along the domain walls (the [110] direction). The loss of long range order in the direction orthogonal to the domain walls most likely arises from the breaking down of the domain wall structures. It is certainly plausible that strip domains of the all-bridge \( (\sqrt{3} \times 2) \) rect phase might form and are separated by higher density \( (\theta > 0.5) \) NO regions in coexistence on the surface. A fluid phase was probably not involved or only existed in a very narrow coverage region between \( \theta = 0.625 \) and 0.5 at the temperature of the LEED observation. In any case, the possibility of a continuous "decompression" of the overlayer can be ruled out on the grounds of IR data indicating the occupation of only localized adsorption sites. As judged from NO thermal desorption spectrum (fig. 2 inset), the ordered NO structures lie in a very narrow temperature region of the \( (\theta, T) \) phase diagram. This makes observation of any intermediate equilibrium structure extremely difficult, if not impossible. For instance, between \( \theta = 0.75 \) and 0.625, a direct \( 2 \times 2 \) to \( 8 \times 2 \) conversion could not be produced by simply annealing the overlayer due to our limited temperature stability. Thus we do not rule out the possibility of additional ordered NO superstructures.

At this point, it is interesting to compare the two adsorption systems, CO and NO on Pd(111), in order to gain further insight into the formation of ordered overlayers. Both molecules follow a similar adsorption sequence on Pd(111), i.e., initial adsorption at three-fold hollow sites, then conversion to two-fold bridge sites at intermediate coverage and finally adsorption onto atop sites. At \( \theta = 0.5 \), the c(4 \times 2) structure involves exclusive bridge site occupation for both CO and NO. Increasing the NO coverage beyond \( \theta = 0.5 \) leads to occupation of the atop sites, as evidenced by IR vibrational data [7]. However, exclusive bridge site occupation is maintained for CO up to a coverage of \( \theta = 0.6 \), allowing a series of phase/antiphase domain structures to develop between \( \theta = 0.5-0.6 \) [27]. Thus for NO the energy gain due to atop site occupation at \( \theta > 0.5 \) seems to be offset (at least partially) by the reduction in intermolecular repulsion, most likely with relaxation at atop sites resulting in a more uniform
NO packing. In addition, the higher vibrational entropy factor associated with the soft frustrated translational mode at atop sites [28] may also contribute to the lowering of the system free energy. The above criteria are obviously not satisfied for CO in the coverage range \( \theta = 0.5-0.6 \). The binding energy difference between bridge- and atop-CO must still be large enough to dominate the overlayer binding site selection. This fundamental difference between adsorbed NO and CO also extends to saturation coverage (\( \theta = 0.75 \)), where all the NO occupy atop sites while only 1/3 of the CO occupy atop sites. Clearly, the details in binding energy difference at various adsorption sites, together with the strength of intermolecular repulsion, dictate the behavior of the overlayer at equilibrium. A thorough understanding about the dynamical behavior of the overlayer also requires knowledge about the adsorption potential energy surface. Such complete characterization of adsorbate systems, although still rare, has indeed begun to emerge [23,24,28].

In summary, we have observed a new ordered overlayer NO superstructure on Pd(111). A phase/antiphase domain structural model has been shown to provide a satisfactory interpretation to LEED and vibrational IR measurements.

Acknowledgment

We acknowledge with pleasure the support of this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

References

[20] The integrated IR band intensity ratio of the 1744/1736 pair to the 1586 band is 2.4: 1. No quantification attempt was made due to the non-linearity involved at high adsorbate coverage and adsorbate relaxation from high-symmetry sites.