

LETTERS

Rational Design of Interfacial Structure: Adsorbate-Mediated Templating

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In this letter we show that it is possible to guide the formation of a novel non-close-packed xenon structure on a stepped nickel surface using an intentionally atomically patterned substrate. By first defining the symmetry and desired dimensions of the underlying superlattice, we successfully template the targeted rare-gas overlayer. Such templating effects, in which the corrugation and structure of the interface can be tuned by prior adsorption of an adsorbate, should be a general route to the formation of new self-organizing interfacial nanoscale structures.

Introduction

The interaction of rare gases with single-crystal surfaces has been a topic of much interest over the past three decades.¹ These systems have served as a testbed for refining our ideas on adsorption dynamics, structure formation, and low-dimensional phase behavior. Adsorption characteristics of xenon in particular have been widely examined, including an abundance of studies on smooth and complex metallic, semiconducting, and insulating substrates. Particular emphasis has been placed on elucidating the phenomena which lead to ordering on (111) metallic surfaces; the geometric simplicity and theoretical tractability of these surfaces facilitates this effort. These studies have shown that xenon typically forms a close-packed $(\sqrt{3}\times\sqrt{3})R30^\circ$ superlattice, governed by a delicate balance of interadsorbate and adsorbate–substrate interactions. In this letter we show that it is possible, using an intentionally atomically patterned surface, to guide the formation of a novel *non-close-packed* xenon structure in which the rare-gas overlayer is templated by the symmetry of the underlying interface. We believe this procedure to be generally applicable to the rational design of custom interfaces and materials.

We have studied both xenon on Ni(977), a stepped surface with (111) terraces (Figure 1a), and xenon on Ni(977) with hydrogen preadsorbed in a (2×2) -2H overlayer (Figure 1b). Low-energy electron diffraction (LEED) results presented in this letter show that this surface supports a commensurate $p(2\times 2)$ -Xe structure that is highly reinforced by a templating preadsorbed hydrogen overlayer. There are many coadsorption phase diagrams exhibiting unusual symmetries in the literature which are well-reviewed by Over.² These systems involve pairs of chemisorbed species that drastically alter the electronic structure of the surface as opposed to our system in which an initially chemisorbed phase imposes its symmetry onto a subsequently deposited physisorbed phase. Also, others have successfully used massively reconstructed surfaces to affect the final xenon symmetry,^{3,4} but our procedure invokes a more subtle and general effect—the preadsorbed hydrogen, not the substrate, serves to corral the xenon atoms into a novel structure.⁵

While novel xenon structures have limited application given their low temperature and inertness, this templating technique can be generalized to other, more practical systems. The ability to selectively engineer the effective symmetry of a surface would enable the creation of an abundance of new nanoscale technologies. One obvious application, given an adsorbate that self-

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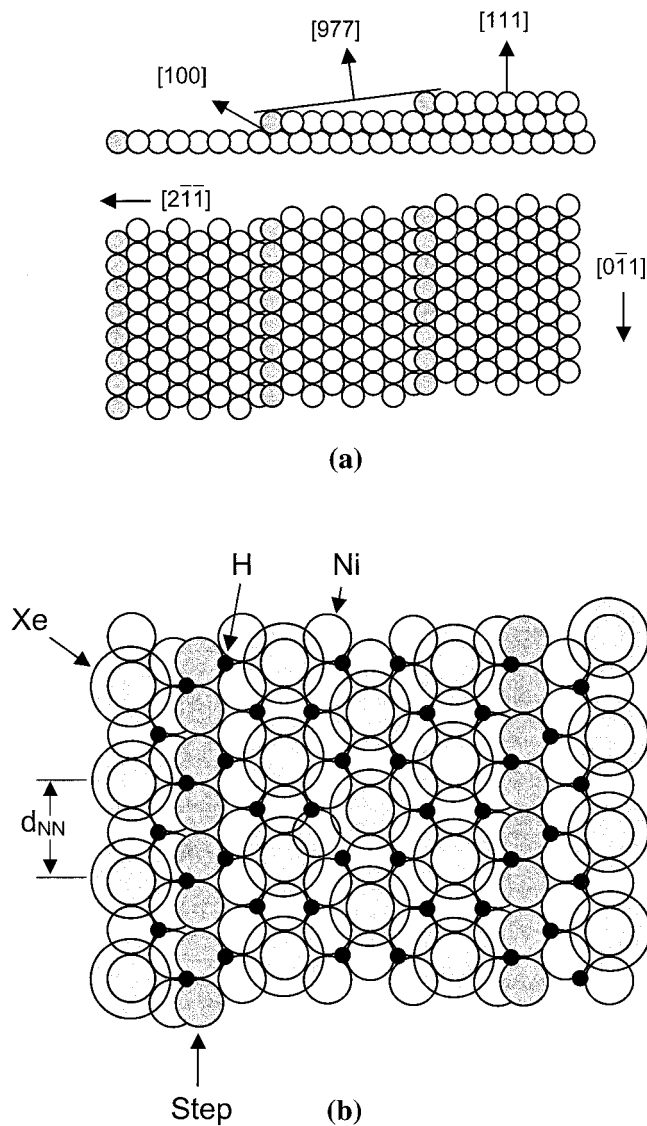


Figure 1. (a) A schematic of the Ni(977) surface as viewed from the side and from above. The surface consists of (111) terraces that are eight atoms wide and separated by single atom high (100) steps. (b) A schematic of a proposed structure where a $p(2 \times 2)$ -Xe overlayer nestles within the open domains of a (2×2) -2H hydrogen overlayer on Ni(977). All atoms are drawn to scale using appropriate van der Waal radii. Note that the xenon atoms sit at nickel on-top sites within nests created by the hydrogen layer. The nearest neighbor distance for xenon (d_{NN}) is 4.98 Å.

assembles into discrete rows, is nanowire patterning. Another straightforward use would be to employ an ordered overlayer to lock further adsorbates in place, functionally inhibiting surface diffusion. Such a system could, for example, slow the formation of oxide islands and therefore enhance corrosion resistance. A more advanced application might be the use of a masking template to engineer the spacing of long-chain organic monolayers for rational design of size-sensitive sensors. A further function of selective two-dimensional templating would be epitaxial growth of three-dimensional structures.⁶ The key to all of these advances is first understanding the fundamental interactions of adsorbates with both surfaces and other adsorbates, especially those that lead to unusual and well-ordered structures.

Experimental Section

These experiments were carried out in an ultrahigh vacuum (UHV) chamber equipped with appropriate surface characteriza-

TABLE 1. Summary of Width Parameters Obtained by Fitting Fractional Order LEED Spots for Xe/Ni(977) and Xe/H/Ni(977)

system	LEED spot	width (Å ⁻¹)	coherence length (Å)	average coherence length (Å)*
Xe/Ni(977)	(0 1/2)	1.05	5.98	9.43 ± 2.41
	(1/2 0)	0.55	11.38	
	(0 1/2)	0.70	9.03	
	(1/2 0)	0.72	8.69	
	(1/2 1/2)	0.52	12.06	
Xe/H/Ni(977)	(1/2 1/2)	0.19	33.04	39.34 ± 9.10
	(0 1/2)	0.12	51.27	
	(1/2 0)	0.13	46.81	
	(0 1/2)	0.20	31.41	
	(1/2 0)	0.18	35.09	
	(1/2 1/2)	0.20	32.10	
	(1/2 1/2)	0.10	65.43	

*Excluding (1/2 1/2) spot, see text.

tion tools as described elsewhere.⁷ Hydrogen and xenon were dosed by backfilling the chamber with partial pressures ranging from 5×10^{-8} to 2×10^{-7} Torr. The Ni(977) crystal used in these studies was cleaned by repeated cycles of sputtering with 1 kV Ne⁺ ions followed by annealing at 1000 K until C and S levels were below our Auger detection limit. Surface crystallinity was confirmed with helium and low-energy electron diffraction.

Results and Discussion

We will now present LEED results showing a marked difference, both qualitative and quantitative, between xenon adsorbed on clean Ni(977) and xenon adsorbed on Ni(977) with an ordered hydrogen underlayer. These results, including diffuse background and diffraction spot analyses, show that xenon forms only a marginally ordered $p(2 \times 2)$ phase on clean Ni(977) whereas it forms a remarkably well-arranged $p(2 \times 2)$ structure in the presence of a preadsorbed hydrogen template. Xenon ($n \times 2$) overlayers have been observed previously, but only on surfaces more corrugated than (111), namely Ag(001)⁸ and Cu(110).⁹ A poorly ordered $p(2 \times 2)$ -Xe overlayer on Ni(977) can be obtained by simply backfilling the chamber with xenon at a partial pressure of 5×10^{-8} Torr as the crystal cools from 100 to 76 K. Note that while xenon desorbs from Ni(111) at 71 K,¹⁰ this overlayer does not desorb until 85 K. We chose to operate in the temperature regime near the desorption temperature because it is the most sensitive to ordering effects, i.e., it is in this thermal range that enhanced order imposed by an underlayer should be most notable.

A $p(2 \times 2)$ -Xe LEED pattern taken at an energy of 125 eV is shown in Figure 2a. Photographs of the LEED pattern were digitized to facilitate analysis of spot profiles. There is streaking in the $\langle 2\bar{1}\bar{1} \rangle$ direction associated with the stepped surface; the spot widths in this direction involve a convolution of domain coherence length and step diffraction. Therefore, we chose to study spot widths in an orthogonal direction ($\langle 0\bar{1}\bar{1} \rangle$). Deconvolution of the line shapes into a Gaussian instrument function (extracted from integer order spots) and a Lorentzian spot profile with a linear background yielded widths for the true overlayer line shapes. Representative fits of spot profiles are shown in Figure 2. Width parameters from the fits for some (2×2) spots are listed in Table 1 along with their respective real-space coherence lengths. Note that the poorly ordered xenon domains which form on the clean metal are quite small, less than 10 Å, or approximately two xenon unit cells. Introducing regular steps

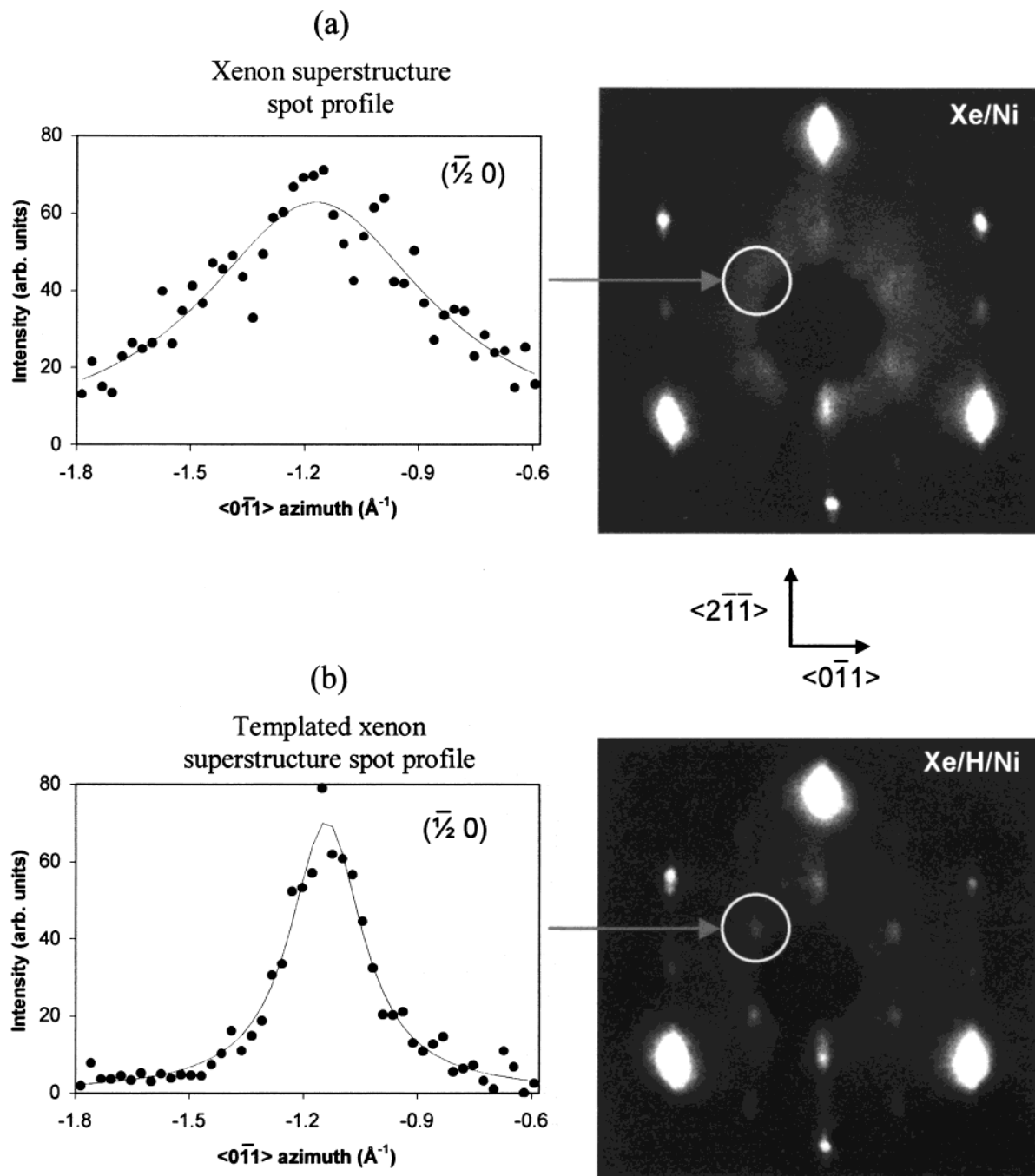


Figure 2. LEED patterns at $E = 125$ eV and substrate $T = 75$ K of (a) Xe/Ni(977) and (b) Xe/H/Ni(977). Overlayer spots of $p(2 \times 2)$ symmetry can be seen together with the substrate spots. Representative best fit line shapes in the $\langle 0, 1, 1 \rangle$ direction with a linear background subtracted are shown for the $(\frac{1}{2}, 0)$ fractional order spot. Note the striking difference in the inner hexagonal assemblage of spots between the two images. Multiple scattering effects convoluted with the geometry of the LEED gun with respect to the macroscopic surface normal reduce the number of mirror planes and cause apparent enhancement of some spots.

to this system shifts the energetics allowing a $p(2 \times 2)$ -Xe rather than the typical $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Xe to form.

We have recently studied the H/Ni(977) phase diagram and have a reliable algorithm for forming a well-ordered (2×2) -2H overlayer.¹¹ This particular system was deliberately selected because its honeycomb structure provides an accessible array of nickel on-top sites for the xenon atoms having the targeted symmetry and dimensions (Figure 1b). After preadsorbing this overlayer, a subsequent application of the xenon dosing procedure described above also results in a $p(2 \times 2)$ -Xe superstructure. A LEED pattern of this structure, obtained using the same parameters as before, is presented in Figure 2b. This

pattern differs both qualitatively and quantitatively from that for adsorption on the clean metal. A visual inspection of the LEED photographs clearly reveals the diffuse nature of the xenon spots on clean Ni(977) relative to the same spots from the surface containing preadsorbed hydrogen. Notice that the diffuse background, a measure of disorder, is significantly lower with hydrogen present. To quantify this change, background levels averaged over the entire pattern were compared. Xenon on bare Ni(977) has a diffuse background 25% higher than that for xenon on preadsorbed hydrogen.

More convincing evidence for overlayer templating can be drawn from the actual superlattice spot widths. Diffraction peaks

analogous to those chosen from the Xe/Ni(977) pattern were fit, and the resulting parameters compared in Table 1. *Clearly, the (2×2) spots become much narrower when a hydrogen overlayer is present.* With one exception, the inner $p(2\times 2)$ -Xe spots on the hydrogen-modified surface are four times narrower than those from the bare nickel surface. The one deviation from this trend, the $(\frac{1}{2}\ \frac{1}{2})$ spot, appears brighter as a product of the geometry of the LEED optics with respect to the crystal. Yet even this spot is still twice as sharp in the presence of hydrogen. The ordered xenon domains are significantly larger, approximately by a factor of 4, when hydrogen is present. Domain sizes have increased from a modest 9.4 to 39.3 Å, or from two to eight xenon unit cells.

In Figure 1b, this surface is schematically depicted with appropriate atomic van der Waals radii. We propose an interwoven arrangement of the two overlayers in which the hydrogen hexagonal cells shepherd the xenon atoms into an otherwise unfavorable (21% lattice expansion from the close-packed arrangement) atomic spacing. *That is, the hydrogen has imposed its (2×2) symmetry on the xenon, thereby templating the novel nanoscale structure.* It is worth noting that this schematic places the xenon at on-top sites, a commonly favored coordination for xenon adatoms.¹²

Shepherding is a consequence of the increased surface electronic corrugation induced by hydrogen preadsorption. Helium atom scattering experiments performed by Gross and Rieder¹³ determined the corrugation of bare Ni(111) to be 0.01 Å. This remarkably smooth face becomes significantly more corrugated with a (2×2)-2H overlayer. For this system, the electronic corrugation is 0.16 Å from a nickel atom peak to a hydrogen atom peak.¹³ Each hydrogen honeycomb (Figure 1b) can then serve as a nest for a xenon adatom. An approximate measure of the energetic magnitude of this templating effect comes from a calculation of the Lennard-Jones adatom–adatom interaction energy:

$$V_{AA} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

where r is the distance between adatoms and the parameters ϵ and σ for gas-phase xenon are 24.87 meV and 3.885 Å, respectively.¹⁴ Gibson et al. have demonstrated that these gas-phase values are only slightly perturbed on metal surfaces.¹⁵ Using this form for the lateral potential, the pair interaction

energy associated with a $(\sqrt{3}\times\sqrt{3})R30^\circ$ xenon structure is 3.80 meV more stable than a $p(2\times 2)$ structure on Ni(111). Expanding the xenon nearest neighbor distance from 4.13 to 4.98 Å by introducing a regular array of steps with a preadsorbed, ordered hydrogen overlayer results in a 20% increase in the xenon–xenon Lennard-Jones interaction energy—a thermodynamic shift significant enough to reverse the stability of the two competing superlattice symmetries.

Conclusions

Our results have shown that one can engineer the symmetry and dimensions of a desired atomic scale structure by using a preadsorbed guiding overlayer. Tuning the corrugation and structure of substrates can be used to induce the formation of novel interfaces. The templating phenomenon described here suggests a universal route to building new rationally constructed and self-organizing two- and three-dimensional structures.

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