Hydrogen-Induced Self-Organized Nanostructuring of the Ir(100) Surface

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We show that the Ir(100) surface forms a new nanostructure in a self-organized way when its reconstructed equilibrium surface is exposed to hydrogen. Scanning tunneling microscopy and quantitative low-energy electron diffraction retrieve that a long-range ordered superlattice of defect-free Ir chains with average lateral spacing of 1.36 nm and micrometer lengths develops. This can be used as a template for the formation of other nanostructures as is demonstrated.

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It has become common knowledge that nanostructured materials exhibit a wealth of new properties which might be used in applications. The most well known device is the modern computer hard-disk read-head which relies on the giant magnetoresistance effect appearing in arrays of magnetic and nonmagnetic layers alternating on the nanoscale. While this nanostructuring is perpendicular to the surface, recent interest has focused also on lateral surface structuring to produce materials of further reduced dimensionality. They consist of one-dimensional stripes (quantum wires) or zero-dimensional dots (quantum dots) aimed to be regularly arranged with spacings on the nanoscale. They can be produced by manipulation using a scanning probe tip, but due to its much higher speed self-organization of such structures is preferred. This has been successful in producing dot arrays, taking advantage of, e.g., periodic stress patterns existing on certain surfaces. For the formation of one-dimensional structures usually stepped surfaces are applied, in particular, when atomically thin wires are aimed for. Surfaces slightly miscut with respect to a high symmetry plane (so that they exhibit periodic parallel steps) are used as a template, whereby the deposited atoms arrange along the step edges (e.g., Refs. [1,2]). Self-organization comes into play (in most cases on semiconductors) when the surface undergoes step-bunching processes. Recent reviews of the field can be found in, e.g., Refs. [3–6].

In this Letter we present an alternative way to produce a nanostructured surface in a self-organized way. We also show that it can serve as template for the formation of further nanostructures via decoration of the linear structural elements formed. We use the (5 × 1) reconstructed Ir(100) surface which is shown to restructure upon exposure to hydrogen. This produces linear atomic chains of macroscopic length with practically no defects and with a lateral order which can be tuned to be almost perfect. While we will eventually demonstrate that the chains can be in fact decorated by, e.g., iron atoms so that chemically composite nanowires are formed, the main focus of the Letter is to illuminate the restructuring process, the lateral arrangement, and order of the developing atomic chains, and the crystallographic structure of the nanostructured surface. For this we apply the scanning tunneling microscope (STM) together with quantitative low-energy electron diffraction (LEED). By this powerful combination of real and reciprocal space methods we can also resolve some questions left open in earlier investigations of hydrogen adsorption on Ir(100) [7–9].

The experiments were performed in an apparatus equipped with a LEED optics and an STM as described in detail earlier [10]. Also, the same Ir(100) crystal was used which, due to its excellent alignment accuracy ($\leq 0.1°$), exhibits huge terraces of up to micrometer size. It exhibits the typical (5 × 1)-hex reconstruction appearing in two mutually orthogonal domains [10]. Figure 1(a) displays the corresponding ball model as confirmed by earlier LEED work [11–14] and STM [14,15]. There is a quasihexagonal top layer wherein 20% more atoms are accommodated than in a bulk layer. This produces a geometrical misfit, so that the top layer becomes buckled as shown in Fig. 1(b) (deeper layers also buckle [14], but this is unimportant here). The most surface protruding atoms correspond nicely to the atoms resolved in the STM [Fig. 1(c)]. Every five substrate unit cells the buckled layer fits to the substrate equivalent to the (5 × 1) symmetry of the LEED pattern [Fig. 2(a)].

Upon hydrogen adsorption at low temperatures ($T < 180$ K) the (5 × 1) symmetry of the LEED pattern remains unchanged *as well as* the energy-averaged

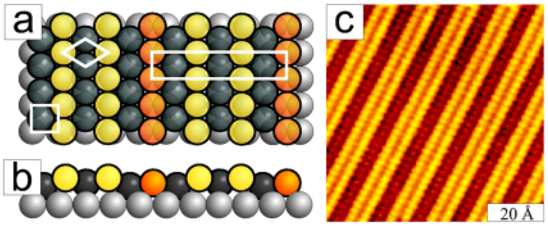

FIG. 1 (color online). Model of Ir(100)-(5 × 1)-hex in (a) the top and (b) the side view. The unit meshes of the bulk layer (quadratic), the top layer (quasihexagonal), and the overall (5 × 1) unit mesh are also given. Panel (c) displays the STM image of Ir(100)-(5 × 1)-hex with the surface protruding atoms resolved.

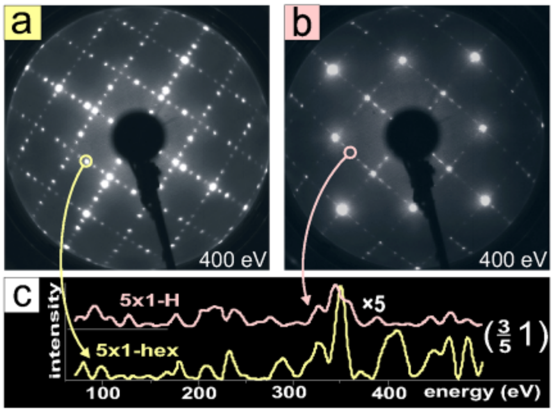

FIG. 2 (color online). LEED patterns of (a) Ir(100)-(5 × 1)-hex and (b) Ir(100)-“(5 × 1)”-H at 400 eV and (c) comparison of their $(\frac{3}{5}\ 1)$ spot spectra.

intensity level of fractional order beams relative to integer order beams ($r^{\mathrm{hex}}_{5\times1} = \langle I_{\mathrm{frac}}\rangle/\langle I_{\mathrm{int}}\rangle \approx 0.6$). This is even at exposures as high as 100 L H_2 [1 L (langmuir) = 10^{-6} Torr · sec]. Additionally, the spectral intensity features only modestly change, indicating that the strong (5 × 1)-hex reconstruction largely persists. Yet, the situation changes dramatically when hydrogen is made to adsorb at $T > 180$ K or when the low temperature adsorption phase is annealed. Figure 2(b) displays the LEED appearance of the hydrogen covered phase as prepared by exposure to 50 L H_2 at 300 K and compares it to the (5 × 1)-hex phase (a). Again the (5 × 1) symmetry of the LEED pattern persists *but* the fractional order beam intensities fall drastically ($r^{\mathrm{H}}_{5\times1} \approx 0.04$). Additionally, the spectra of the fractional order beams change markedly [Fig. 2(c)]. This proves that the new phase [in the following named “(5 × 1)”-H because the real-space periodicity will turn out to be (5 × 1) only on average] is not a residuum of an uncomplete lifting of the surface reconstruction towards the unreconstructed (1 × 1) phase (as assumed earlier [7]) but is a phase on its own. Also, upon hydrogen deposition we never could produce a pure (1 × 1) nor a pure (3 × 1) diffraction pattern as reported also in earlier work [8,9].

The STM immediately resolves the atomic nature of the “(5 × 1)”-H phase. For the preparation described above, Figs. 3(a) and 3(b) show (for one of two orthogonal domains) that the “(5 × 1)”-H phase is characterized by monoatomic Ir chains residing on a quadratic substrate as the zooming in between two chains shows [Fig. 3(c)]. Evaluation of the chain density yields that it corresponds *exactly* to a 20% coverage equivalent to the density of excess atoms in the former hexagonal layer. This suggests that the chain atoms were expelled from this layer (in a collective way forming chains) whereby the atoms left rearrange to form a bulklike layer. There are patches were the chains form a regular (5 × 1) superlattice [Fig. 3(b)], but on a larger scale the arrangement is (5 × 1) only on average. This is demonstrated by the distribution displayed in Fig. 3(d) [along the line in Fig. 3(a)]. In the image shown, 70% of the chain spacings are $5a$ (with $a = 2.72$ Å the Ir surface lattice parameter), while spacings with $3a$ and $7a$ occur with 15% probability. This is equivalent to (5 × 1) long-range order with, however, some short range disorder built in and, as mentioned, indicated by the apostrophes in the name “(5 × 1)”-H. We also point out that contrast and apparent atomic heights in the STM images may be influenced by the presence of hydrogen. Yet, though we have no information about its coverage and adsorption sites, this should not affect the identification of the nanowires. Also, as shown below all structural quantities will be derived by quantitative LEED.

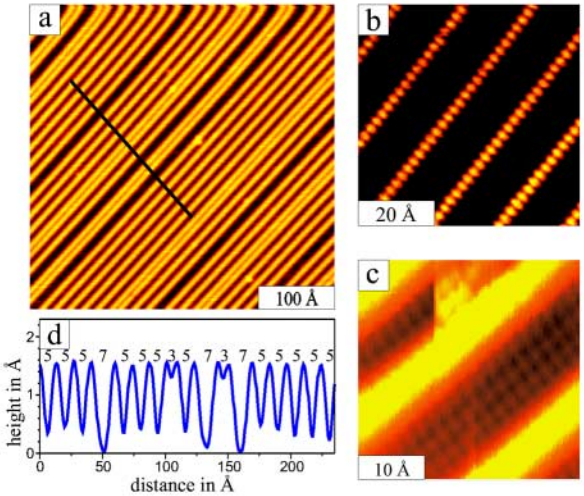

FIG. 3 (color online). (a) STM image of the “(5 × 1)”-H phase [prepared by exposure of the clean (5 × 1)-hex surface to 50 L H_2 at 300 K] with the tip in (b) and (c) closer to the surface. Panel (d) provides the chain distribution along the line displayed in (a).

No other spacings than $3a$, $5a$, and $7a$ are observed. Their relative weights (with $3a$ and $7a$ always equally probable) depend sensitively on the preparation conditions. So, exposure of the (5 × 1)-hex phase to 200 L H_2 at 90 K and subsequent annealing at 300 K leads to a chain arrangement as displayed in Fig. 4(a), i.e., with only 20% $5a$ spacings but 40% $3a$ and $7a$ spacings so that large patches of the surface exhibit a (10 × 1) superlattice. Consequently, the corresponding LEED pattern [Fig. 4(b)] exhibits spots also at 1/10 order positions as demonstrated by the spot profile on the right of Fig. 4(b). On energy average the 3/10 and 4/10 together with the 6/10 and 7/10 order spots are the most intense ones (in agreement with a kinematically calculated structure factor) and so one could be inclined to take this a (3 × 1) superstructure. Also, due to the prevailing not strictly periodic arrangement of the chains the LEED pattern (and profile) owns also some streaky features. This was also observed in the work reporting the above mentioned (3 × 1) superstructure [8,9] and so our results appear

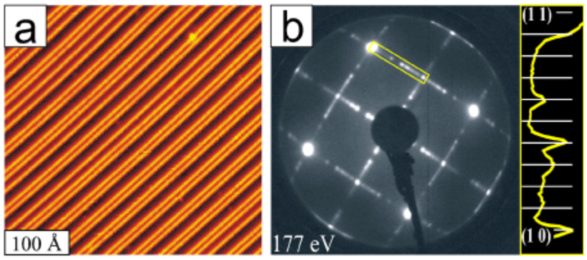

FIG. 4 (color online). (a) STM image of the H-induced phase prepared by exposure of (5 × 1)-hex to 200 L H_2 at 90 K and subsequent annealing at 300 K. An (only partially) ordered (10 × 1) phase results. (b) Corresponding LEED pattern (177 eV). The intensity profile of the spots framed is attached on the right.

to be rather close to that, though our interpretation is different.

The long-range regular arrangement of the chains can be understood by the initial (5 × 1)-hex reconstruction and by the top layer buckling involved. As evident from STM images of intermediate states of the transition, i.e., incompletely restructured surfaces [e.g., Fig. 5(a)], the chains are right at those positions where the most surface protruding rows of the (5 × 1)-hex reconstruction had been located [bright rows in Figs. 1(b) and 1(c)]. So it is reasonable to assume that exactly one of these two rows is expelled, so that the 20% excess atoms accommodated in the quasihexagonal top layer are removed, allowing the remaining atoms to rearrange to a quadratic (bulklike) lattice plane. Of course, by symmetry arguments the two rows (with a spacing of about 2a) are equivalent and so, not surprisingly, the developing “(5 × 1)”-H phase exhibits not only chain spacings of 5a but also of (5 ± 2)a, as observed indeed. Of course, this requires the chains to be immobile after ejection which is reasonable, because the collective diffusion of a chain as a whole is unlikely. The fact that the distribution of chain spacings is not fully random and depends on the details of preparation is indicative for the existence of (possibly hydrogen mediated) chain-chain interactions.

The restructuring of the surface upon hydrogen exposure must be due to the adsorption on the new surface being energetically favoured over that on the (5 × 1)-hex phase. Yet, as atoms have to be expelled from the hexagonal top layer, atomic bonds have to be broken equivalent with our observation that the transition is an activated process. As at surface defects some bonds are already broken, a smaller activation energy applies there so that the transition most likely starts at defects as observed, indeed. The activation energy should be smallest for the two atoms protruding already out of the surface so that only these atoms are ejected. Once one of these atoms is ejected, the other one can rearrange together with the remaining atoms to quadratic (bulklike) order stabilized by adsorbed hydrogen. The atom ejected starts a new or continues an already existing chain and thus is equivalent to a new surface defect adjacent to the next (5 × 1)-hex unit cell. Also, this breaks the equivalence of the two protruding atoms within that cell and triggers the ejection to proceed in a ziplike process as indicated in Fig. 5(b).

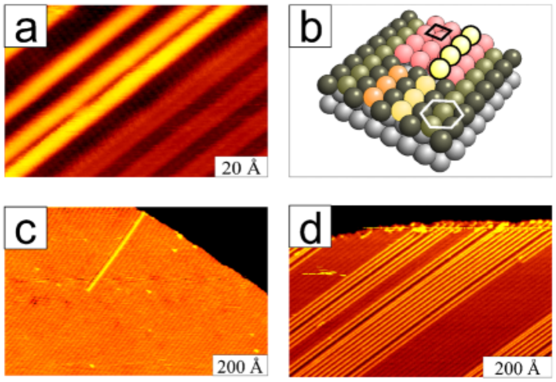

FIG. 5 (color online). (a) High-resolution STM image of an incompletely restructured surface. (b) Model according to which an Ir chain is expelled in a ziplike process (see text). (c), (d) STM images for intermediate states of the (5 × 1)-hex → “(5 × 1)”-H transition for increasing exposure to H_2 at room temperature. The transition predominantly starts at surface defects as step edges.

The described scenario of the (5 × 1)-hex → ”(5 × 1)”-H transition is corroborated by STM observations. Figures 5(c) and 5(d) demonstrate that the transition exclusively starts at surface defects like step edges or domain boundaries. Local defects were found as starting points, too. As a consequence, the rate with which the transition proceeds should depend significantly on the history of the sample, i.e., the density of surface defects present, as is observed indeed. Also, when there is not enough hydrogen offered to stabilize the developing (1 × 1) structured patches, the transition stops at a certain point (the images in Fig. 5 were taken at such points). For these intermediate states the LEED intensities are superpositions of those of the initial (5 × 1)-hex and final “(5 × 1)”-H structures. The latter develops at the expense of the first and, in agreement with the STM images, there are no different intermediate structures. This phase coexistence is indicative for the phase transition being of first order. The scenario described seems to be similar to the transition hex → (1 × 1) of Pt(100) for which computational simulations were published recently [16]. Applying a modified embedded atom method, the lifting of the reconstruction by exposure to CO is shown to proceed in the same way as suggested above for H/Ir(100), i.e., by ejection of atomic chains from the hexagonal top layer. Yet, the final state is a CO covered (1 × 1) phase rather than a reorganized (5 × 1) phase as in the present case.

In order to retrieve the crystallographic structure of the “(5 × 1)”-H phase, its LEED intensities were recorded for normal incidence of the primary beam and the sample at 90 K. Using a computer controlled video technique [17,18] spectra of 7 integer and 21 fractional order beams (symmetrically nonequivalent at normal incidence) were collected (total data base width: $\Delta E = 8516$ eV). The

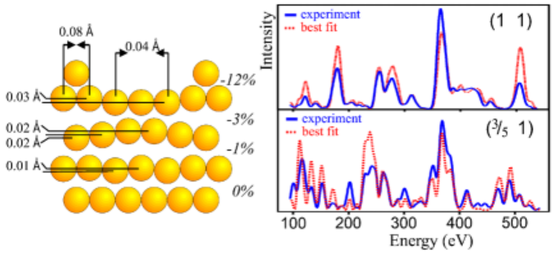

FIG. 6 (color online). Left: Crystallographic model of the "(5 × 1)"-H phase with the best-fit structural parameters given as resulting by LEED structure determination. The interlayer distances are given by the percentage change with respect to the bulk layer spacing, $d = 1.92$ Å. Right: Comparison of experimental and best-fit calculated data for two selected beams.

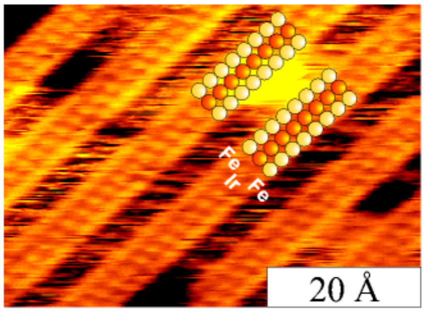

FIG. 7 (color online). Fe-Ir-Fe sandwich nanowires as resulting by deposition of Fe on the "(5 × 1)"-H surface. At two locations the iron and iridium atoms making up the chains are identified by atomic spheres.

perturbation method TensorLEED [17,19,20] was applied to calculate model intensities whereby the TensErLEED programme package [21] was used. As a reference for the structural perturbation the information from STM was used, i.e., a (5 × 1) superlattice of Ir chains residing on the bulklike terminated substrate. Then the atomic positions within the chain and the first three substrate layers were varied in a way that the C_{2v} symmetry of the (5 × 1) unit mesh was preserved. The structural search applied (using a frustrated annealing procedure [22] and applying the Pendry R-factor R_P [23]) quickly finds the best-fit structure whose structural parameters are displayed on the left of Fig. 6. The chain superlattice induces some buckling in the substrate. We point out that we cannot resolve the position of the hydrogen atoms as their scattering strength is negligible compared to that of Ir. The minimum R-factor value is $R_P = 0.27$ and the corresponding visual comparison between the best-fit model intensities and experimental data is given in Fig. 6 for two selected beams. Finally the reader should note that in the "(5 × 1)"-H phase described only one atom per (5 × 1) unit cell scatters into fractional order spots (if we neglect the small buckling of substrate layers), while in the (5 × 1)-hex phase as much as six surface atoms contribute. This accounts for the considerable decrease of intensities in the (5 × 1)-hex → "(5 × 1)"-H transition.

The superlattice of Ir chains with their nanoscale spacing (1.36 nm) can be used as a template to produce new nanostructures. As a first example, Fig. 7 displays the result obtained via decoration of both sides of the Ir chains by Fe. Chemically sandwiched quantum wires form whereby atomic rows of magnetic and nonmagnetic material alternate. This sandwich model is quantitatively confirmed by a LEED analysis similar to that described above. The fit, which is of excellent quality ($R_P = 0.20$), shows that on average 90% of the Ir chain atoms are Fe decorated on both their sides, with the Fe-Ir bond length (2.68 Å) close to the sum of the elements' covalent radii (2.60 Å). Possibly, the sandwich chains own interesting magnetic properties. Their measurement is planned as well as the use of a slightly miscut Ir(100) sample by which one of the two orthogonal reconstruction domains should be suppressed, so that sandwich chains develop only in one direction.

In conclusion, we have shown that (5 × 1)-hex reconstructed Ir(100) can be made to restructure by exposure to hydrogen. By self-organization a superlattice of atomic Ir chains develops with a spacing on the nanometer scale. This can be used as a template to create new other nanostructures by decoration.

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