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Laterally nanostructured cobalt oxide films on Ir(100)

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Our recent investigation of a c(4 × 2)-periodic cobalt-oxide layer growing on Co/Ir(100) (but not on bare Ir) has been extended to the oxide growth on Co covered Ir(100)-(5 × 1)-H. When only the patches between the latter's nanospaced Ir wires are Co covered—so that the oxide forming in the next layer is in contact with both Co patches and Ir wires—the c(4 × 2) phase grows only above Co; i.e., it is interrupted by the Ir wires equivalent to a nanostructured oxide. This proves that the chemical influence of the substrate on the oxide growth is highly local.

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Recently we have reported that the growth of epitaxial CoO films on the Ir(100)-(1 × 1) surface switches from the [111] direction on the bare iridium substrate to the [100] direction when one or several monolayers (ML) of cobalt are introduced as interlayer(s) between the oxide and iridium.[1] The switch is initiated by the development of a c(4 × 2) periodic oxide layer which turns out to be a single CoO(100) layer with Co vacancies in a c(4 × 2) arrangement and which is a precursor for further [100] type growth. It was also shown by means of calculations using density functional theory that the development of the c(4 × 2) phase is energetically favorable only with at least one ML of Co underneath it; i.e., it is the chemical impact of the underlying binding partner which stabilizes the phase. The reader should note that structurally equivalent c(4 × 2) phases were found also for other oxide/substrate combinations.[2–9]

The question arising upon our previous finding is, how local is this interface chemistry driven effect? In order to answer this we prepared a suitably patterned substrate so that the growth of CoO domains in contact with either bare iridium or an interfacing Co layer is possible. We find that the growth of the c(4 × 2) phase on the latter is interrupted even by iridium chains of monoatomic width, i.e., the growth switch is extremely local. Also, by covering the patterned substrate completely with cobalt—i.e., by several MLs of it and so fully shielding the chemical influence of iridium (but not removing the geometric buckling and the strain imposed by the structurally corrugated interface)—the c(4 × 2) phase remains. This is further proof that the chemical binding dominates the growth in this system and not the strain within the growing film.

We apply low-energy electron diffraction (LEED) as well as scanning tunneling microscopy (STM) as described in detail in previous papers.[10–15] LEED and STM data were recorded at liquid nitrogen and room temperature, respectively. For the preparation of the patterned iridium substrate we profit from the structural flexibility of Ir(100). Its native reconstruction, which exhibits a close packed hexagonal top layer,[16,17] can be transformed to the unreconstructed (1 × 1) phase by chemical treatment.[17–19] On this surface the above-mentioned switch of oxide growth from the [111] direction to the [100] direction by the introduction of one or several Co layers between the oxide and the substrate has been investigated.[1]

On the other hand, the Ir surface can also be transformed (and stabilized) by hydrogen adsorption to a differently reconstructed surface. In the latter iridium wires of monoatomic width reside in (5 × 1) periodicity on the otherwise unreconstructed substrate.[20] As outlined earlier the spacing between the Ir wires can be $3a$, $5a$, and $7a$ (with $a = 2.715$ Å the in-plane lattice parameter of Ir), whereby the average spacing is $5a = 1.36$ nm. So, the fivefold periodicity is only on average as illustrated in Fig. 1(a). Figure 1(b) displays a section of it whereby the inset is zoomed-in, showing that between the Ir wires there is (1 × 1) order. If on this phase 0.7–0.8 ML of Co is deposited the adatoms fill the space between the iridium wires thus forming a Co_4Ir surface alloy as indicated schematically in Fig. 1(c) and illustrated by the STM image in Fig. 1(d). The phase has been investigated in detail in previous papers.[21,22] The reader should note that the H atoms move to the new surface and desorb already at about room temperature. The surface alloy remains stable up to much higher temperatures.

So, when a cobalt oxide layer is grown on the phase shown in Fig. 1(d) it is—varying laterally—locally in contact with both interfacing Co and Ir species. The oxide was prepared, in the first step, by deposition of about 1.7 ML of Co on the Ir(100)-(5 × 1)-H phase illustrated schematically in Fig. 2(a). In a second step this was oxidized by exposure to an oxygen partial pressure of about 5×10^{-9} mbar at 50°C and for 2.5 min whereby the hydrogen atoms had already desorbed. Experience with the preparation procedure of the oxide on Ir(100)-(1 × 1) (Ref. 1) tells that this results in the oxidation of only the top Co layer as indicated in Fig. 2(b).

After annealing of the so prepared oxide at 400 °C a (5 × 4) periodic LEED pattern results as presented in Fig. 3(a). This is consistent with the fivefold periodicity of the Ir substrate in one direction and the fourfold periodicity of the c(4 × 2) phase in the other direction. In the STM image [Fig. 3(b)] we observe chainlike features with spacings of $3a$, $5a$, and $7a$, whereby the average is $5a$. These are exactly the spacings of the Ir wires on the Ir(100)-(5 × 1)-H phase [Fig. 1(a)] which therefore can be assumed to lie in the middle below the chains (accordingly the fivefold periodicity is again only on average). In between the chains we find stripes of oxides with an appearance very similar to that of the c(4 × 2) phase on Co/Ir(100)-(1 × 1). The height profile along the line inserted in the STM image is given in Fig. 3(c). Based on the experience with the c(4 × 2) phase on Ir(100)-(1 × 1) (Ref. 1) we can safely assume that peaks in the profile correlate to cobalt ions only. This allows us to draw a ball model for the Co ions which, by adding the Co/Ir

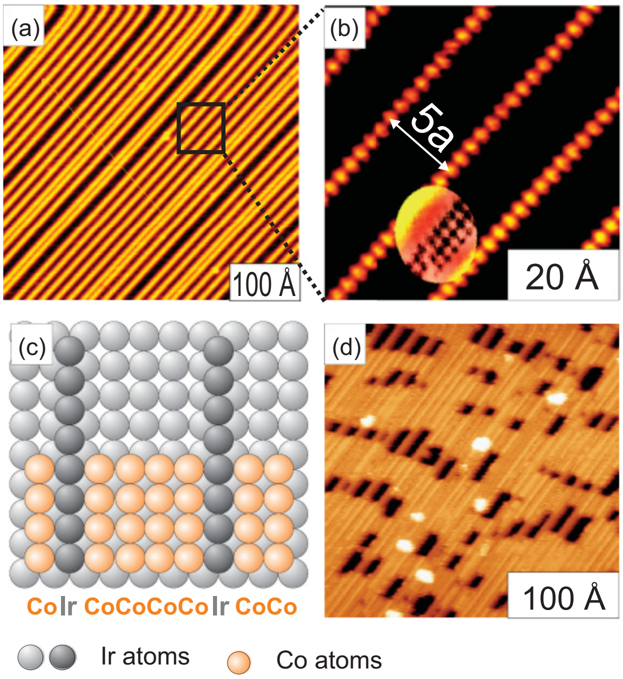

FIG. 1. (Color online) (a) Large scale STM pattern of Ir(100)-(5 × 1)-H (19 mV, 0.59 nA). Panel (b) shows an enlarged image (4.6 mV, 0.77 nA) with a zoomed-in image inserted that shows that between the Ir wires the structure is (1 × 1). The quantity $a = 2.715$ Å is the in-plane lattice parameter of Ir(100). Panel (c) shows a ball model of the clean and Co covered substrate in its upper and lower part, respectively. Panel (d) displays the STM image of the (5 × 1)-H phase when covered with about 0.75 ML of Co (2.1 V, 0.50 nA).

substrate and the oxygen ions, results in the model given in Fig. 3(d). As is obvious, in the profile line in Fig. 3(c) Co ions are missing in the oxide stripes between the Ir wires consistent with the missing ions in the homogeneous c(4 × 2) phase. Also, Co double chains appear to reside above the Ir wires of the substrate on which, presumably, oxygen occupies fourfold sites. So, the (5 × 4) phase is a laterally nanostructured cobalt oxide.

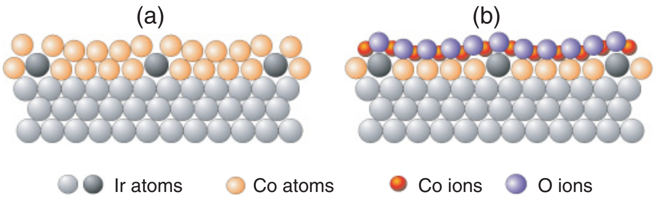

FIG. 2. (Color online) Vertical cut ball models for Ir(100)-(5 × 1)-H covered with 1.7 ML of Co (a) before and (b) after partial oxidation.

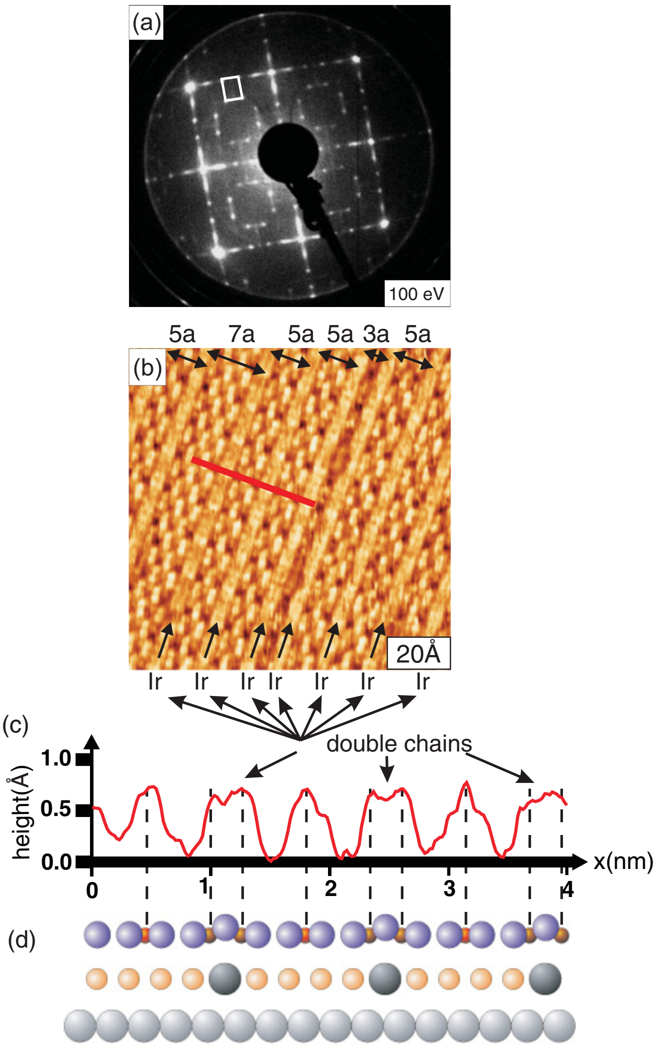

FIG. 3. (Color online) (a) LEED pattern [with the (5 × 4) unit cell inserted] and (b) STM image (2.3 mV, 11 nA) of the partially oxidized 1.7 ML Co/Ir(100)-(5 × 1)-H phase. Panel (c) displays the STM profile along the line in panel (b) and panel (d) provides a ball model (see text).

The final proof that the structure between the Ir wires (i.e., in the areas above the Co patches of the substrate) is identical to the oxidic c(4 × 2) precursor phase quantitatively determined on Co/Ir(100)-(1 × 1) (Ref. 1) comes by the comparison of STM images and quantitative LEED data. Figure 4(a) resumes an STM image from Ref. 1 with Co species indicated by red balls. In Fig. 4(b) an enlarged part of the STM image in Fig. 3(b) is displayed for comparison again with the Co species highlighted. As is obvious the appearance in the areas between the Co double chains above the Ir wires at the interface is very much the same as well as that of the (local) noncentered unit cell. Of course, the real unit cell is of (5 × 4) size as illustrated in the ball model in Fig. 4(c). The Co double chains above the Ir wires introduce a phase shift in the fivefold, i.e., $[0\bar{1}1]$ direction, so that c(4 × 2) units on both sides of the Co double chains are in antiphase condition. Accordingly, the (1/2 3/4) spot of the homogeneous c(4 × 2) phase splits into the (2/5 3/4) and (3/5 3/4) spots of the (5 × 4) phase. As a consequence, the sum of their intensities should be largely dominated by the local c(4 × 2) structure. Indeed, the comparison of the related intensity spectra [Fig. 4(d)] reveals rather similar spectra, indicative for similar structural features of the extended and local c(4 × 2) phases. Yet, while in the homogeneous c(4 × 2) phase the Co coverage is 0.75 ML [relative to the (1 × 1) Ir substrate] it is, due to the dense double chains and the phase shift between neighbored c(4 × 2) patches, 0.85 ML in the (5 × 2) phase. Adding the 0.8 ML deposited between the Ir wires of the Ir substrate comes close

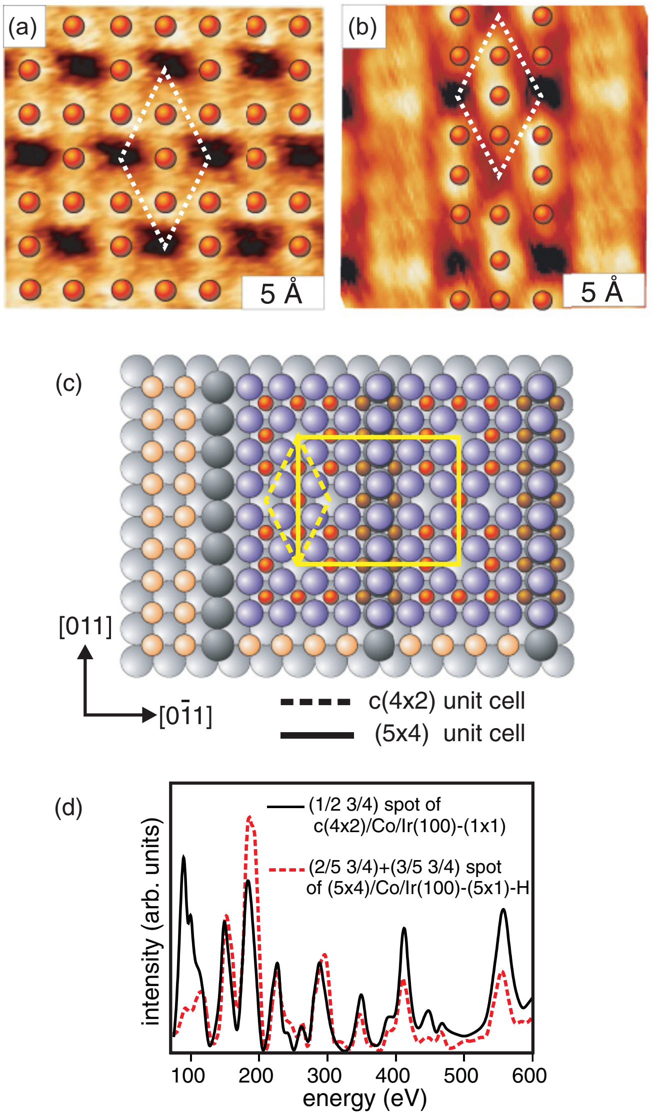

FIG. 4. (Color online) STM images with Co species and the (local) c(4 × 2) cell inserted (a) of the homogeneous c(4 × 2) phase on Ir(100)-(1 × 1) (Ref. 1) (0.12 V, 8.1 nA) and (b) of the (5 × 4) phase (2.3 mV, 11 nA) as part of Fig. 3(b). Panel (c) provides a ball model of the (5 × 4) phase whereby Co species in a c(4 × 2) arrangement and within the double chains are differently shaded. Panel (d) compares LEED spectra of equivalent diffraction spots of the homogeneous c(4 × 2) phase and the (5 × 4) phase.

to the nominal 1.7 ML of Co deposited to form the oxide by partial oxidation.

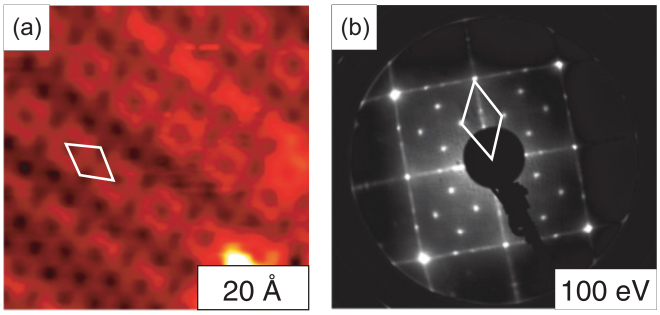

FIG. 5. (Color online) (a) STM image (0.42 V, 0.47 nA) and (b) LEED pattern of a long-range ordered c(4 × 2) oxide layer formed on 2.8 ML of Co film deposited on Ir(100)-(5 × 1)-H.

The final issue we address is the structure resulting from the oxidation of the top layer of a thicker Co film on Ir(100)-(5 × 1)-H, i.e., for the case where the oxide layer is only in direct contact with Co atoms below it and not with iridium atoms. A film of 3.7 ML of Co was deposited on Ir(100)-(5 × 1)-H. Oxidation of the top layer (as described above for the 1.7 ML case) results in the STM image and the LEED pattern displayed in Fig. 5. As is obvious from the diffraction pattern, there is a pure and well-ordered c(4 × 2) phase [the weak additional spots originate from the (5 × 1) periodic interface and the equally periodic buckling imprinted into the overlying film]. As can be taken from the STM image the surface is slightly corrugated. The corrugation amplitude amounts to 0.15 Å. This value is only a little smaller than that determined by quantitative LEED for a 2.8 ML Co film on Ir(100)-(5 × 1)-H in a separate work (0.19 Å) (Ref. 23) in which it was shown that the corrugation stems from the Ir wires on the Ir bulk. As the c(4 × 2)-periodic oxide layer contains 0.75 ML of Co the cobalt film below amounts to a coverage close to that of the 2.8 ML Co film investigated. Consequently, we can conclude that the oxide layer is carpetlike arranged on the buckled Co/Ir substrate decorating it with a slightly reduced corrugation amplitude as frequently happens in such cases.

The results described above are in full agreement with our recent finding that cobalt oxide in contact with cobalt atoms at the interface to the iridium substrate forms a c(4 × 2) periodic oxide with Co vacancies. This holds even for only nanosized lateral patches whereby the local structure is very similar to that of the laterally homogeneous phase found on Ir(100)-(1 × 1). Yet, the c(4 × 2)-periodic oxide does not develop when directly in contact with Ir. This holds even for the atomic-width Ir wires; i.e., the influence of the interface chemistry is extremely local. As a consequence, using an already nanopatterned substrate as Ir(100)-(5 × 1)-H a laterally nanostructured cobalt oxide can be formed. The chemical influence of Ir [inhibiting the formation of the c(4 × 2) phase] is effectively shielded when covered by Co. Though our results are obtained for a special nanopatterned substrate the findings described might also apply to other systems, e.g., for artificially nanostructured metals or alloy surfaces in combination with suitable oxides.

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