Oxygen-induced nano-faceting of $\text{Re}(11\bar{2}1)$

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Abstract

We report results from a detailed study of oxygen-induced faceting of $\text{Re}(11\bar{2}1)$ using low energy electron diffraction (LEED). Depending on conditions for reaction with oxygen, the initially planar $\text{Re}(11\bar{2}1)$ surface evolves sequentially to form zigzag chains consisting of $(01\bar{1}0)$ and $(10\bar{1}0)$ facets that coexist with stepped $(11\bar{2}1)$ plateaus; three-sided pyramids exposing $(01\bar{1}0)$, $(10\bar{1}0)$ and $(33\bar{6}4)$ facets; a faceted surface with five facets including $(01\bar{1}0)$, $(10\bar{1}0)$, $(11\bar{2}2)-(2\times 1)$, $(01\bar{1}1)-(2\times 1)$ and $(10\bar{1}1)-(2\times 1)$; and four-sided pyramids exposing $\{01\bar{1}0\}$ and $\{01\bar{1}1\}-(2\times 1)$ facets. We have observed reversible morphological transitions between the faceted surfaces and discovered that each intermediate facet in the evolutionary chain contains microscopic structural elements of the preceding and following facets, which may provide a natural explanation for the microscopic mass transport pathways in the morphological evolution. Scanning tunneling microscopy (STM) data confirm the morphology of faceted surfaces and give complementary information to LEED results.

Keywords: rhenium, faceting, mass transport, oxygen, morphology

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1. INTRODUCTION

The morphology and the physical properties of solid surfaces can influence each other in intricate ways. For example, dc current-induced electromigration can lead to step bunching on surfaces[1-4], anisotropic effects on vicinal surfaces can lead to unexpected behavior in magnetic overlayers[5, 6], and nanoscale rearrangements of metal surfaces can result in drastic changes in their reactivity. As an example of this latter point, nanoscale metal particles, often used in catalytic applications, are known to change their shape and size under reaction conditions[7-10], which in turn affects their activity and selectivity. These changes are attributed to the strong interaction between adsorbates (reactants, intermediates) and metal nanoparticles, which is related to adsorbate-induced morphological evolution (i.e. faceting) of metal surfaces[11-14]. It is therefore critical to understand not only how thermodynamic properties, such as anisotropy of surface free energy, can drive surface morphological changes, but also how these changes may come about on the atomistic level. A powerful and highly-controlled way to approach these questions is to study adsorbate-induced faceting of atomically rough single crystal metal surfaces[15]; faceting occurs when an initially planar surface undergoes a morphological rearrangement exposing new nanoscale crystal faces (facets). Faceted metal single crystal surfaces have been successfully used as nanoscale model systems to study catalytic reactions[12, 16, 17], and as templates for synthesis of nanostructured model electrocatalysts[18].

Adsorbate-induced faceting of metal surfaces, which include both planar and curved (tip) metal surfaces[11-15, 17-27], has been studied extensively in recent years. However, among the previous studies, an atomic-level understanding of how the mass transport necessary to form facets occurs is lacking. One approach to investigating this question is to choose an adsorbate-substrate system that can sustain metastable states that can be easily studied and serve as snapshots along the evolution route from the initial planar surface to the final faceted surface[15].

In this paper we focus on just such a system: O-induced faceting of the $\text{Re}(11\bar{2}1)$ surface. The reaction of adsorbates with Re surfaces is of increasing interest[18, 28-31] because Re-based catalysts have been used in many important reactions including ammonia synthesis[32], olefin metathesis[33], carbon nanotube growth[34] and thiophene hydrodesulfurization[35]. In particular, ammonia synthesis catalyzed by rhenium single crystal surfaces under reaction conditions similar to those used in industry is highly structure sensitive with reactivity increasing in the order: $\text{Re}(0001) < \text{Re}(01\bar{1}0) < \text{Re}(11\bar{2}0) < \text{Re}(11\bar{2}1)$ [32]. Our previous studies revealed that nitrogen can induce faceting of $\text{Re}(11\bar{2}1)$ upon annealing in NH_3 to form two-sided ridges consisting of $(13\bar{4}2)$ and $(31\bar{4}2)$ facets[15, 31], and the high reactivity of $\text{Re}(11\bar{2}1)$ toward ammonia synthesis may be related to the formation of the nanoscale facets during the reaction. Another previous study found that adsorption of oxygen on the closely related $\text{Re}(12\bar{3}1)$ surface can induce formation of various facets upon annealing[15, 27]. Among the facets that appear on that surface, the $(11\bar{2}1)$ facet is unique in that it persists when the oxygen coverage is low but disappears at high oxygen coverage[15, 26, 27]. This behavior suggests that by starting with a planar $\text{Re}(11\bar{2}1)$ surface, it may be possible to observe intermediate facets by tuning the reaction condition with oxygen, which in turn can lead to a microscopic understanding of Re mass transport pathways. Moreover, $\text{Re}(11\bar{2}1)$, which is an atomically rough surface with four atomic layers exposed as shown in the hard-sphere models of Figs. 1(a) and 1(b), has higher symmetry than $(12\bar{3}1)$ [15, 27], so the faceted surfaces that evolve from $(11\bar{2}1)$ should also have higher symmetry than those from $(12\bar{3}1)$. As a result, identification of the facet orientations and investigation of the atomic-level structural connections between different sets of facets sustained on this surface are simplified. Figure 1(c) shows a portion of the stereographic projection plot of

the hcp lattice on the $(11\bar{2}0)$ plane, where the $(11\bar{2}1)$ orientation is labeled by a hollow circle. There are two surface terminations on $\text{Re}(11\bar{2}1)$ [36].

2. EXPERIMENTAL METHODS

All experiments were performed in two ultra-high vacuum (UHV) chambers with base pressures of about 1×10^{-10} Torr. One chamber contains Auger electron spectroscopy (AES), low energy electron diffraction (LEED) instrumentation and a quadrupole mass spectrometer (QMS)[37], and the other chamber contains LEED, AES, QMS and a McAllister scanning tunneling microscope[26, 27]. A $\text{Re}(11\bar{2}1)$ single crystal, 99.99% pure and aligned within 0.5° of the $(11\bar{2}1)$ orientation, was used in the study; it is $\sim 8\text{mm}$ in diameter and $\sim 1\text{mm}$ thick. The Re crystal was cleaned by cycles of e-beam heating in oxygen (1×10^{-7} Torr) followed by flashing in UHV to above 2000K, and the cleanliness of the Re surface was checked by AES. The $\text{Re}(11\bar{2}1)$ surface was exposed to oxygen either at 300K or at elevated temperatures by backfilling the chamber. The oxygen pressure during adsorption on $\text{Re}(11\bar{2}1)$ was monitored using an uncalibrated Bayard-Alpert ionization gauge and the total exposures were reported in Langmuir (L, $1\text{L} = 1 \times 10^{-6}$ Torr·s). The presence of surface oxygen was confirmed by AES. The sample temperature was measured either by a C-type (W-5 at.% Re/W-26 at.% Re) thermocouple spot-welded to the back of the Re crystal or by an infrared pyrometer.

LEED was used to establish the presence of faceting on the $\text{Re}(11\bar{2}1)$ surface and to determine facet orientations[15, 27]. The specular (zero-order) LEED beam of a planar surface (or a facet) is fixed as a function of E_i ; diffracted beams converge on the specular as E_i increases[38]. In the standard LEED configuration, because the incident electron beam is normal to the planar surface, the specular beam is located in the center of the screen. If the planar

surface becomes faceted, the incident electron beam is not normal to either of the facets, so the specular beams hit the screen at positions that are characteristic of the facet orientations. The corresponding LEED pattern, superposition of diffraction contributions from individual facets, converges on these specular beams with increasing E_i , and can be analyzed to reveal the orientations and atomic structures of the facets[15, 27]. In this study, the LEED patterns were taken from the sample cooled to room temperature.

STM measurements were performed to provide complementary information of the faceted surfaces in real space, including local arrangements and size distribution of the facets. All the STM measurements were made at room temperature in the constant-current mode. The typical sample bias is between 0.5 - 1.2V and the tunneling current is between 0.6 – 1.0nA.

3. RESULTS

3.1. Partially faceted $\text{Re}(11\bar{2}1)$: emergence of the $(01\bar{1}0)$ and $(10\bar{1}0)$ facets

Fig. 2(a) shows a typical LEED pattern of the clean $\text{Re}(11\bar{2}1)$ surface. All of the diffraction spots are from the planar surface (spots A and C are indicated for future reference) and no evidence for reconstruction is found even after the surface is annealed in UHV at temperatures up to 2000K. Adsorption of oxygen at 300K also does not induce any reconstruction, and the LEED pattern (not shown) looks almost same as Fig. 2(a) except for a slight increase of the background signal associated with random adsorption of oxygen.

Fig. 2(b) shows a LEED pattern of the $\text{Re}(11\bar{2}1)$ surface exposed to 10L O_2 at 300K followed by annealing at 1000K for 2 minutes. Diffraction spots associated with planar $(11\bar{2}1)$ regions persist (e.g., spots A and C) and the dashed parallelogram denotes the unit cell of the diffraction pattern from the planar $(11\bar{2}1)$ regions; these diffraction spots converge to the center

of the screen (marked by a yellow circle) as E_i increases. However, new features (e.g. spots B and D) also appear. When E_i increases, the spots move as indicated by red arrows, toward two points marked by red circles, outside the LEED screen. These new points of convergence indicate the formation of two new facets that coexist with the $(11\bar{2}1)$ regions, i.e. the initially planar $(11\bar{2}1)$ surface has become partially faceted. Moreover, the diffraction spots from the facets are streaky, indicating that the facet size along the direction of the streaks is smaller than 10 nm, the transfer width of LEED[15, 27]. Because the diffraction spots from the two facets have a symmetry axis along the $[\bar{1}\bar{1}26]$ direction, here we only show how to identify one of the facets by analyzing the motion of its representative diffraction spots.

In Fig. 2(b), the four diffraction spots A-D always stay on a straight line (marked by a yellow line to guide the eye) for different electron beam energies. This behavior indicates that the reciprocal rods corresponding to these four spots are located in a same plane parallel to the incident electron beam[15], a property that is better illustrated in an Ewald-sphere construction of the LEED pattern shown in Fig. 2(c): the normal vector of this plane, perpendicular to the AC direction, is the axis of the crystallographic zone containing $(11\bar{2}1)$ and the facet. Because the LEED pattern from $(11\bar{2}1)$ resembles its crystal lattice pattern in real space rotated by 90° (see Figs. 2(b) and 2(d)), the zone axis can then be identified as $[\bar{2}113]$, and thus the facet must be in the $\langle\bar{2}113\rangle$ zone. Notably, since the specular beam of the facet is located outside the LEED screen, the tilt angle of the facet must be larger than 30° , half of the screen acceptance angle. Among all the surfaces in the $\langle\bar{2}113\rangle$ zone, $(01\bar{1}0)$ is the most plausible facet candidate because it is the most close-packed surface near $(11\bar{2}1)$ (see Fig. 1(c)) and because it has a tilt angle of 34.1° with respect to $(11\bar{2}1)$. Due to the symmetry between the two facets mentioned above, the

other facet must be $(10\bar{1}0)$. This assignment is confirmed by a kinematical LEED simulation shown in Fig. 2(e).

3.2. Fully faceted $\text{Re}(11\bar{2}1)$: emergence of the $(33\bar{6}4)$ facet

When $\text{Re}(11\bar{2}1)$ is exposed to 60L of O_2 at 300K followed by annealing at 1000K for 2 minutes, important changes in the LEED pattern have been observed, as seen in Fig. 3(a). At first glance, the pattern appears similar to the LEED pattern in Fig. 2(b), however, in Fig. 3(a) *the four spots labeled as A-D no longer lie along a straight line*. This deviation from a straight line persists even when the electron beam energy changes, indicating that the surface morphology has changed from that in Fig. 2(b). Although in Fig. 3(a) spots B and D are still from the $(01\bar{1}0)$ facet, spots A and C are no longer from the $(11\bar{2}1)$ region but from a new facet. On the other hand, since the deviation is subtle, the new facet must be vicinal to $(11\bar{2}1)$ with a small tilt angle. The new facet is then identified as $(33\bar{6}4)$ (see Ref. [39] for details of the $(33\bar{6}4)$ facet identification), which is confirmed by the agreement between kinematical LEED simulations and the experimental LEED patterns, as shown in Fig. 3(b). The spatial relationship between the $(11\bar{2}1)$ substrate and the three observed facets of $(01\bar{1}0)$, $(10\bar{1}0)$ and $(33\bar{6}4)$ is shown in Fig. 1(c). Upon further annealing the surface at 1200K in UHV for 2 minutes, the LEED pattern in Fig. 3(a) reverts to that in Fig. 2(b) due to desorption of a small amount of oxygen [40]. This is the first observation of reversible morphological transition between two types of faceted single crystal metal surfaces. Upon subsequent annealing the surface at 1300K in UHV for 2 minutes, the LEED pattern reverts to that seen in Fig. 2(a) (data not shown), indicating that the surface returns to its original planar geometry.

3.3. Further evolution of fully faceted $\text{Re}(11\bar{2}1)$: emergence of the $(11\bar{2}2)$ -(2×1) and $\{01\bar{1}1\}$ -(2×1) facets

The LEED results presented in the previous section show that the morphology of a faceted $\text{Re}(11\bar{2}1)$ surface depends on the initial oxygen exposure at 300K before annealing at 1000K in UHV: as oxygen exposure increases (thus oxygen coverage increases [27]), the surface morphology evolves from a partially faceted surface to a fully faceted surface consisting of three-sided pyramids. However, with this facet preparation procedure, the maximum amount of surface oxygen is limited by the saturation coverage at 300K[26, 27]. In order to go beyond this limit and explore the possibility of other facet formation, a new preparation procedure is employed: the $\text{Re}(11\bar{2}1)$ surface is exposed to O_2 while being heated at high temperatures and then the sample is cooled to 300K before LEED measurements. This new facet preparation procedure has proven effective in our previous study of oxygen-induced faceting of $\text{Re}(12\bar{3}1)$ [26].

The effect of an elevated substrate temperature during oxygen adsorption is two-folds: first, for given oxygen pressure, surface coverage is temperature dependent owing to the balance of oxygen adsorption-desorption processes; second, the substrate temperature affects atomic mobility, which in turn drives the kinetics of facet formation.

Fig. 4 shows LEED patterns taken after a planar $\text{Re}(11\bar{2}1)$ surface is dosed with 10-120L O_2 at 1000K (except that Fig. 4(c) is for oxygen exposure at 900K). When the oxygen exposure is 10L, the LEED pattern shown in Fig. 4(a) looks similar to that of Fig. 2(b): the surface is partially faceted with $(01\bar{1}0)$ and $(10\bar{1}0)$ facets coexisting with planar $(11\bar{2}1)$ regions. Since the Re crystal is kept at 1000K for 20 minutes, much longer than the 2 min annealing time used for Fig. 2(b), the diffraction spots from the facets in Fig. 4(a) are less streaky than those in Fig. 2(b),

indicating that the facet size increases with longer annealing time. When the oxygen exposure is increased to 30L, the LEED pattern is shown in Fig. 4(b): the surface is completely faceted with $(01\bar{1}0)$, $(10\bar{1}0)$, $(33\bar{6}4)$ and two unknown facets, which will be identified as $(01\bar{1}1)-(2\times 1)$ and $(10\bar{1}1)-(2\times 1)$ later. With further increase of oxygen exposure to 60L, the LEED pattern changed slightly from that of Fig. 4(b), indicating possibility of new facet formation (data not shown). This new facet can be better prepared by exposing the surface to 60L O_2 at 900K, which brings more pronounced difference as shown in Fig. 4(c). Four of the five facets occurring in Fig. 4(b) remain intact in Fig. 4(c) except that the $(33\bar{6}4)$ facet is replaced by a new facet: $(11\bar{2}2)$, which is (2×1) reconstructed with the unit cell labeled by a dashed white rectangle in Fig. 4(c) (see Fig. 5.7 and related text in Ref. 15 for the details of the identification of the $(11\bar{2}2)-(2\times 1)$ facet). When the oxygen exposure is increased to 120L, the LEED pattern is shown in Fig. 4(d): the diffraction spots from $(11\bar{2}2)$ completely disappear and the surface is fully faceted with $(01\bar{1}0)$, $(10\bar{1}0)$ and the two unknown facets. Further increasing oxygen exposure to as high as 300L does not bring any new surface structures (LEED pattern not shown)[15]. Analysis of the spatial arrangement of the diffraction spots from the two unknown facets with respect to those from the $\{01\bar{1}0\}$ facets reveals that the two unknown facets are (2×1) reconstructed $(01\bar{1}1)$ and $(10\bar{1}1)$ facets (see Ref. [41] for details of the identification of the $(01\bar{1}1)-(2\times 1)$ and $(10\bar{1}1)-(2\times 1)$ facets). This assignment is confirmed by the kinematical LEED simulation shown in Fig. 4(e). Fig. 4(f) shows a schematic diagram of the Ewald-sphere construction for the right-most arc in Fig. 4(d).

When the substrate temperature is increased to 1100K during a 120L oxygen exposure, the faceted $(11\bar{2}1)$ surface reverses the morphological evolution course from that in Fig 4(d) due to desorption of some oxygen[40]: it becomes completely faceted with $(01\bar{1}0)$ $(10\bar{1}0)$ and $(33\bar{6}4)$ facets as shown in Fig. 5(a), which resembles Fig. 3(a). Note that in Fig. 3(a), the diffraction

spots labeled as A, B and C are not on a straight line, which is the signature feature distinguishing $(3\bar{3}64)$ facets from $(11\bar{2}1)$ region. This reversed morphological evolution continues when $\text{Re}(11\bar{2}1)$ is exposed to 120L of O_2 at 1200K due to further desorption of some oxygen [40]. The corresponding LEED pattern in Fig. 5(b) now resembles Fig. 2(b), indicating that the $\text{Re}(11\bar{2}1)$ surface becomes partially faceted and covered by $(01\bar{1}0)$ and $(10\bar{1}0)$ facets coexisting with the $(11\bar{2}1)$ region. The LEED patterns shown in Fig. 4 and Fig. 5 once again demonstrate the reversible transition between different types of faceted $\text{Re}(11\bar{2}1)$ surfaces.

3.4. Morphology of the stable facets

To investigate the local real-space surface structures (morphologies) of the faceted surfaces, STM measurements were conducted. Here we focus on the morphologies of the faceted surface with four stable facets formed with the highest amount of surface oxygen: $(01\bar{1}0)$, $(10\bar{1}0)$, $(01\bar{1}1)$ and $(10\bar{1}1)$, where $(01\bar{1}0)$ and $(10\bar{1}0)$ also appear on the partially faceted surface as evidenced by the LEED patterns in Fig. 2(b), Fig. 4(a) and Fig. 5(b). Figure 6(a) is a typical STM image taken from a $\text{Re}(11\bar{2}1)$ surface exposed to 10L O_2 at 300K followed by annealing at 1000K for 2 minutes, i.e. the same preparation that generates the LEED pattern shown in Fig. 2(b). The image shows flat regions or plateaus, separated by zigzag chains. The orientation of the plateaus is confirmed as $(11\bar{2}1)$ by atomic resolution STM images, such as the one shown in Fig. 6(b), obtained from one of the plateaus. The zigzag chains are actually made of narrow bands of $(01\bar{1}0)$ and $(10\bar{1}0)$ facets, which is evident in Fig. 6(c), a 3D representation of Fig. 6(a). The orientations of the two facets are confirmed by the tilt angles between the facets and the $(11\bar{2}1)$ plateaus, and by the angle between the facet edges. Figure 6(d) shows the cross-section profile along a line passing points A and B in Fig. 6(a); the profile segment AB corresponds to the

(01 $\bar{1}$ 0) facet, which has a slope angle of $32 \pm 2^\circ$, in good agreement with the ideal tilt angle of 34.2° between the (01 $\bar{1}$ 0) (or (10 $\bar{1}$ 0)) and (11 $\bar{2}$ 1) planes. Moreover, the experimentally determined angle between the facet edges of $55 \pm 2^\circ$ also agrees well with the ideal value of 54.2° as calculated from the spatial relationship between (01 $\bar{1}$ 0), (10 $\bar{1}$ 0) and (11 $\bar{2}$ 1). Note that in Fig. 6(a) each (11 $\bar{2}$ 1) plateau is shaded in several different colors, indicating that the (11 $\bar{2}$ 1) plateau contains atomic height steps. Since (01 $\bar{1}$ 0) and (10 $\bar{1}$ 0) facets and (11 $\bar{2}$ 1) region alone cannot retain the macroscopic orientation of the initial (11 $\bar{2}$ 1) surface, these steps cause the local effective orientation of the plateaus to deviate from (11 $\bar{2}$ 1) and allow the surface to retain its macroscopic orientation.

As described above, when the Re(11 $\bar{2}$ 1) surface is exposed to 120L or 300L O₂ at 1000K, it becomes completely faceted with four facets: (01 $\bar{1}$ 0), (10 $\bar{1}$ 0), (01 $\bar{1}$ 1) and (10 $\bar{1}$ 1). Figure 7(a) shows a typical differentiated STM image after Re(11 $\bar{2}$ 1) is exposed to 300L O₂ at 1000K. Four different facets can be identified, and in some regions they meet together to form 4-sided pyramids; one example of the pyramid is marked by an oval in Fig. 7(a). Fig. 7(b) shows an STM image of the four-sided pyramid formed by the four stable facets. Edges between neighboring facets are marked by black lines. The angles between the edges projected on (11 $\bar{2}$ 1) are measured experimentally, while the error bars are estimated on the uncertainty of drawing the edge lines. Fig. 7(c) shows ideal edge arrangement of the pyramid in Fig. 7(b) if formed by (01 $\bar{1}$ 0), (10 $\bar{1}$ 0), (01 $\bar{1}$ 1) and (10 $\bar{1}$ 1) facets. Clearly, the measured angles agree well with their corresponding ideal values.

4. DISCUSSION

Adsorbate-induced faceting is believed to be driven by the increased anisotropy of the surface free energy due to preferential adsorption of the adsorbates on surfaces with certain orientations[42]. The total surface free energy is minimized by forming facets that have lower specific surface free energy than the original planar surface, although the total surface area may increase[12]. Motivated by our work on oxygen-induced faceting of rhenium surfaces[15], using *ab-initio* methods based on density functional theory (DFT), Kaghazchi and Jacob have calculated the surface free energies of both clean and oxygen-covered $(11\bar{2}1)$ as well as facets including $\{01\bar{1}0\}$ and $\{01\bar{1}1\}$ [43, 44]. The calculated phase diagram confirms that upon adsorption of oxygen, a completely faceted surface with $(01\bar{1}0)$, $(01\bar{1}1)$, $(10\bar{1}0)$ and $(10\bar{1}1)$ facets is energetically favored against planar $(11\bar{2}1)$ at $T < 1250\text{K}$. However, the calculations did not include the intermediate facets $(33\bar{6}4)$ and $(11\bar{2}2)$ and thus could not answer an important question: why the morphological evolution of the facets take the path observed experimentally from one to another and eventually form four-sided pyramids containing $\{01\bar{1}0\}$ and $\{01\bar{1}1\}$ facets?

Fig. 8(a) shows schematic models of all the observed faceted structures, and Fig. 8(b) and (c) show hard-sphere models of the metastable facets. A close examination of these models reveals atomic-level connections between them. At low oxygen exposure (thus low oxygen coverage[27]), the surface is partially faceted with $\{01\bar{1}0\}$ facets coexisting with stepped $(11\bar{2}1)$ plateaus. This is understandable since $\{01\bar{1}0\}$ facets have the lowest specific surface free energies among possible facet candidates near $(11\bar{2}1)$ [43, 44]. Furthermore, both LEED and STM measurements show that the $\{01\bar{1}0\}$ facets have narrow width of $\sim 10\text{nm}$, indicating that they can be formed simply by rearrangement of steps on $(11\bar{2}1)$ followed by step bunching; the

mass transport involved is thus minimal. An increase in oxygen exposure (thus increase in oxygen coverage[27]) leads to the emergence of $(3\bar{3}\bar{6}4)$ facets, whose bulk-truncated surface can be regarded as a stepped $(11\bar{2}1)$ surface with the terrace width equal to one $(11\bar{2}1)$ unit cell (Fig. 8(b))[15]. So, from the perspective of mass transport, it is an easy transition from $(11\bar{2}1)$ to $(3\bar{3}\bar{6}4)$, which can occur with local mass transport. With further increasing oxygen exposure, the $(3\bar{3}\bar{6}4)$ facets evolve into $(11\bar{2}2)$ facets predominantly ($\{01\bar{1}1\}$ also emerge but are not fully developed). This transition can be understood in the sense that the bulk truncated $(3\bar{3}\bar{6}4)$ can also be considered as a stepped $(11\bar{2}2)$ surface from a different view angle (Fig. 8(b)). The $(3\bar{3}\bar{6}4)$ facet acts as a transition state between the $(11\bar{2}1)$ surface and the $(11\bar{2}2)$ facets: an increase or decrease of oxygen coverage can trigger $(3\bar{3}\bar{6}4)$ to tilt toward one or the other.

For the last transition from $(11\bar{2}2)$ to $\{01\bar{1}1\}$ at high oxygen exposure, there initially appears to be no direct connection between the structures of these two surfaces, however LEED shows that the $(11\bar{2}2)$ facet exhibits a (2×1) reconstruction. A simple model based on this reconstruction, shown in Fig. 8(c), indicates that if every other row of top-layer atoms along the $[11\bar{2}3]$ direction is removed, the resulting $(11\bar{2}2)-(2\times 1)$ surface contains micro-facets of $(01\bar{1}1)$ and $(10\bar{1}1)$ orientations. At high oxygen exposure, these micro-facets grow in size and eventually evolve into large $(01\bar{1}1)$ and $(10\bar{1}1)$ facets.

5. CONCLUSION

A complicated and reversible morphological evolution has been observed in oxygen-induced faceting of $\text{Re}(11\bar{2}1)$ by LEED. The various morphologies of the faceted surface range from zigzag chains consisting of $(01\bar{1}0)$ and $(10\bar{1}0)$ facets that coexist with stepped $(11\bar{2}1)$ plateaus; three-sided pyramids exposing $(01\bar{1}0)$, $(10\bar{1}0)$ and $(3\bar{3}\bar{6}4)$ facets; a faceted surface with five

different facets including $(01\bar{1}0)$, $(10\bar{1}0)$, $(11\bar{2}2)-(2\times 1)$, $(01-11)-(2\times 1)$ and $(10-11)-(2\times 1)$ facets; to four-sided pyramids exposing $\{01\bar{1}0\}$ and $\{01\bar{1}1\}-(2\times 1)$ facets. Among all the observed facets, $\{01\bar{1}0\}$ and $\{01\bar{1}1\}$ are the stable ones in the sense that they persist at high oxygen exposures. We have shown that there are structural connections between the facets in the reversible morphological evolution: each intermediate facet in the evolutionary chain contains microscopic structural elements of the preceding and following facets. The existence of these microscopic elements reveals how local mass transport can accommodate morphological transitions from one faceted surface to another. Our results are important for understanding the reactivity of Re-based catalysts that operate under oxygen-rich conditions as they may experience shape transformation due to the formation of new facets. This work provides an approach towards understanding mass transport pathways in other catalytically active but morphologically unstable metal surfaces and nanostructures.

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FIGURE CAPTIONS:

Fig. 1. (a) Top and side view of the hard-sphere model of the bulk-truncated $(11\bar{2}1)$ surface with a unit cell marked. (b) Another stacking sequence of the $(11\bar{2}1)$ surface with one more layer of atoms added on top of the surface in (a). (c) Part of the stereographic projection plot of the hcp lattice on $(11\bar{2}0)$. The $(11\bar{2}1)$ surface is labeled by a hollow circle; four crystallographic zones are also labeled for discussion in the text.

Fig. 2. (a) LEED pattern taken at 68eV from a clean and planar $\text{Re}(11\bar{2}1)$ surface. (b) LEED pattern taken at 68eV from a partially faceted $\text{Re}(11\bar{2}1)$ surface after it is exposed to 10L O_2 at 300K followed by annealing at 1000K for 2 min. The inset in the lower right corner of (b) shows a schematic model of the corresponding surface morphology. (c) Schematic diagram of the Ewald-sphere construction corresponding to the diffraction spots A-D in (b). (d) Atomic structure of the $(11\bar{2}1)$ surface oriented in the way that its unit cell resembles that of the diffraction pattern from the $(11\bar{2}1)$ region in (a) and (b) rotated by 90° . (e) Kinematical LEED simulation of (b) based on the 2D lattices of $(11\bar{2}1)$, $(01\bar{1}0)$ and $(10\bar{1}0)$, in which the solid circles are diffraction spots from $(11\bar{2}1)$ and the hollow circles are from $(01\bar{1}0)$ and $(10\bar{1}0)$.

Fig. 3. (a) LEED pattern taken at 68eV from a fully faceted $\text{Re}(11\bar{2}1)$ surface after it is exposed to 60L O_2 at 300K followed by annealing at 1000K for 2 min. Diffraction spots A, C and E are from the $(33\bar{6}4)$ facet and the specular beam of $(33\bar{6}4)$ is marked by a red circle. The inset shows a schematic model of the corresponding surface morphology. (b) Kinematical LEED simulation of (a) based on the 2D lattices of the $(33\bar{6}4)$ and $\{01\bar{1}0\}$ facets.

Fig. 4. LEED patterns taken at 68eV after a $\text{Re}(11\bar{2}1)$ surface is exposed to (a) 10L O_2 at 1000K, (b) 30L O_2 at 1000K, (c) 60L O_2 at 900K, and (d) 120L O_2 at 1000K, respectively. The insets in (a)-(d) show schematic models of the corresponding surface morphology. (e) Kinematical LEED simulation of (d) based on the 2D lattices of the $\{01\bar{1}1\}$ -(2×1) and $\{01\bar{1}0\}$ facets. (f) Schematic diagram of the Ewald-sphere construction for the right-most arc in (d).

Fig. 5. LEED patterns taken at 68eV after a $\text{Re}(11\bar{2}1)$ surface is exposed to (a) 120L O_2 at 1100K, and (b) 120L O_2 at 1200K, respectively. The insets in (a) and (b) show schematic models of the corresponding surface morphology.

Fig. 6. (a) $1000\text{\AA}\times 1000\text{\AA}$ STM image of a partially faceted $\text{Re}(11\bar{2}1)$ surface after being exposed to 10L O_2 at 300K followed by annealing at 1000K. The dashed lines mark the angle formed by the intersection lines between $\{01\bar{1}0\}$ facets and the $(11\bar{2}1)$ terrace. (b) $80\text{\AA}\times 60\text{\AA}$ STM image from the same surface as (a) showing atomic structure of the $(11\bar{2}1)$ terrace. A unit cell of $(11\bar{2}1)$ is labeled by a blue parallelogram. (c) 3D representation of (a) showing the zigzag chains in (a) are actually made of narrow bands of well-defined facets. (d) Cross-section profile along the solid line AB in (a).

Fig. 7. (a) $1000\text{\AA}\times 1000\text{\AA}$ x-slope STM image of a fully faceted $\text{Re}(11\bar{2}1)$ surface after being exposed to 300L O_2 at 1000K. The oval in (a) highlights a 4-sided pyramid formed by four facets;

a schematic model of the pyramid is shown in the lower right corner of (a). **(b)** Experimentally measured angles between the facet edge lines. **(c)** Calculated angles between the facet edge lines.

Fig. 8. **(a)** Schematic models of all the observed faceted structures. **(b)** Hard-sphere model of the $(33\bar{6}4)$ facet. The side view shows two different ways of viewing the same surface. **(c)** Proposed hard-sphere model of the $(11\bar{2}2)-(2\times 1)$ facet.

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- [39] Identification of the $(3\bar{3}\bar{6}4)$ facet. As shown in Fig. 3(a), the specular beam of the new facet has almost zero intensity for different values of E_i , but its position can still be estimated on the basis of the following two observations: 1) since the diffraction spots from the new facet retain the mirror symmetry along the $[\bar{1}\bar{1}26]$ direction, the specular beam must be on the same symmetry axis; 2) the two spots labeled as A and E in Fig. 3(a) move toward each other when E_i increases, indicating that the specular beam is also located on the line connecting these two spots. Therefore, the intersection point between the symmetry axis and the line AE is the specular beam position of the new facet, labeled by a red circle in Fig. 3(a), whose tilt angle with respect to $(11\bar{2}1)$ is then determined to be $\sim 6^\circ$. The diffraction beams from the new facet are similar to those from $(11\bar{2}1)$ because the new facet is vicinal to $(11\bar{2}1)$ and located in the $\langle 1\bar{1}00 \rangle$ zone. Two possible facet candidates in the $\langle 1\bar{1}00 \rangle$ zone are $(22\bar{4}3)$ and $(3\bar{3}\bar{6}4)$, with tilt angles of 7.7° and 5.2° , respectively. However, kinematical simulations of the LEED pattern based on 2D lattices of $(22\bar{4}3)$ and $(3\bar{3}\bar{6}4)$ reveal that only the later gives a good match to the experimental LEED pattern in the main text.
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- [41] Identification of the $(01\bar{1}1)$ and $(10\bar{1}1)$ facets. In Fig. 4(d), among four facets, two of them are the previously identified $(01\bar{1}0)$ and $(10\bar{1}0)$ (see section III. A). To identify the other two unknown facets, we notice the following two characteristics of their diffraction spots: 1) they are also symmetrical along the $[\bar{1}\bar{1}26]$ direction; 2) they always form arcs together with the spots from $(01\bar{1}0)$ and $(10\bar{1}0)$ facets at different electron energies. Five diffraction spots on the right most arc are labeled in Fig. 4(d), among which three are from $(01\bar{1}0)$ (labeled by dashed arrows) and the other two are from one of the unknown facets (labeled by solid arrows). According to the Ewald-sphere construction for LEED shown in Fig. 4(f), diffraction spots on an arc indicate that their corresponding reciprocal rods are located in a same plane that is not parallel to the incident electron beam. This plane is indicated by a grey oval in Fig. 4(f). Because the five reciprocal rods in Fig. 4(f) are perpendicular to their corresponding facets, the crystallographic zone axis (i.e. the intersection line) of the facets, must also be perpendicular to the aforementioned plane that contains the five reciprocal rods. The reciprocal rods corresponding to the three diffraction spots of $(01\bar{1}0)$ are located in the $(2\bar{1}\bar{1}0)$ plane, whose normal direction is $[2\bar{1}\bar{1}0]$. Therefore, one of the unknown facets must be in the $\langle 2\bar{1}\bar{1}0 \rangle$ zone and the other must be in the $\langle \bar{1}2\bar{1}0 \rangle$ zone due to the mirror symmetry. As shown in the stereographic projection plot in Fig. 1(c), $(01\bar{1}1)$ and $(10\bar{1}1)$ are the only probable facet candidates because both are close-packed surfaces and have low

surface free energy; (0001) cannot be the facet orientation because two instead of one unknown facets are observed. Kinematical simulations of the LEED pattern in Fig. 4(e) are performed on the basis of the 2D lattices of $(01\bar{1}0)$, $(10\bar{1}0)$, $(01\bar{1}1)$ and $(10\bar{1}1)$ to confirm the facet orientations. However, a good match between the experimental and simulated LEED patterns can only be achieved by assuming that $(01\bar{1}1)$ and $(10\bar{1}1)$ are (2×1) reconstructed along the $[1100]$ direction. For example, the two beams labeled by solid arrows in Fig. 4(c) are the direct evidence of the (2×1) reconstruction because the distance between them is about half of the value from an unreconstructed $(01\bar{1}1)$ surface.

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Fig. 1

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Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Graphical abstract