OBSERVATION OF A NEW ORDERED STRUCTURE OF OXYGEN ON W(110)

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ABSTRACT

Using both low energy electron diffraction (LEED) and scanning tunneling microscopy (STM), we have made the first observation of a new ordered surface structure of oxygen on W(110). This structure is characterized by the matrix $\begin{pmatrix} 3 & -1 \\ 0 & 5 \end{pmatrix}$ relative to the (1x1) W(110) structure, in which 15 tungsten atoms make up the rectangular unit cell. Based on high resolution STM images, a model for the structure is proposed which includes 6 adsorbed oxygen atoms and has a coverage of 0.40 ML.

INTRODUCTION

The system of oxygen dosed on W(110) has been studied since 1913[1] and its ordered structures characterized by LEED[2,3,4] and STM,[5] in addition to other techniques. Oxygen has been found to form three ordered structures when dosed on W(110) under various dosing conditions. These structures are the (2x1) at 0.50 monolayers (ML), (2x2) at 0.75 ML, and (1x1) at 1.00 ML. In this study, we have confirmed the formation of each of these structures in both LEED and STM measurements. In addition, we have discovered a new fourth structure, which forms at 0.40 ML after an oxygen dose of 3 to 6 Langmuirs (L).

EXPERIMENT

The sample crystals used in the experiment were two tungsten (110) crystals sliced from a boule and polished with a final miscut angle of less than 2° for both. Although the new structure for oxygen on W(110) was observed for both crystals, all data shown here were measured on the same W(110) crystal with the same azimuthal crystal orientation in all experiments. In preparation for LEED or STM experiments, the samples were cleaned using an oxygen-dosing and annealing procedure similar to that found in the literature:[6] the sample is dosed with oxygen at 1.0×10^{-7} torr for 5 minutes, then annealed several times to at least 1900 K using electron beam heating from a cathode heater. The samples were then allowed to cool to approximately 400 K before beginning the oxygen adsorbate dose. The new structure is found to occur at a range of exposures, from 1.0×10^{-7} torr for 30 sec (3 L), to 3.0×10^{-9} torr for 33.33 min (6 L). Typically, the samples are checked with LEED before moving them to the STM chamber for imaging. The chamber base pressure is 1 to 2×10^{-10} torr. The observation of various structures of O on W(110) as a function of dosing pressure has been suggested by another study,[7] and those results will be published elsewhere.

RESULTS

The new structure for O on W(110) was discovered to have the LEED pattern shown in the diagram in Fig. 1(a). The sharpest LEED spots were found at an energy of approximately 13 eV. This new structure often coexists with the (2x1) structure, which can also be created under similar dosing conditions. Moving the sample a few millimeters from side to side can be enough to display strong regions of the new structure adjacent to strong regions of the (2x1) pattern. The real space structure inferred from this LEED pattern is shown in Fig. 1(b) and discussed in more detail in the next section.

After examining the LEED pattern, STM images were measured, such as those shown in Fig. 2. Notice that at least two rotational domains are possible for this structure. The images in Figs. 2(a) and 2(b) were taken in separate STM experiments (i.e., the sample was cleaned and redosed with oxygen between these images) with different dosing conditions. After observing this new structure in approximately 15 different STM experiments, these domains have not been observed to coexist on the same dosed sample. Fig. 2(c) shows a region of (2x1) structure seen in the same experiment as the new structure in Fig. 2(a). Fig. 3(a) shows results from a third experiment which, with its higher resolution, suggests additional features in the inner structure of the unit cell, as discussed below.

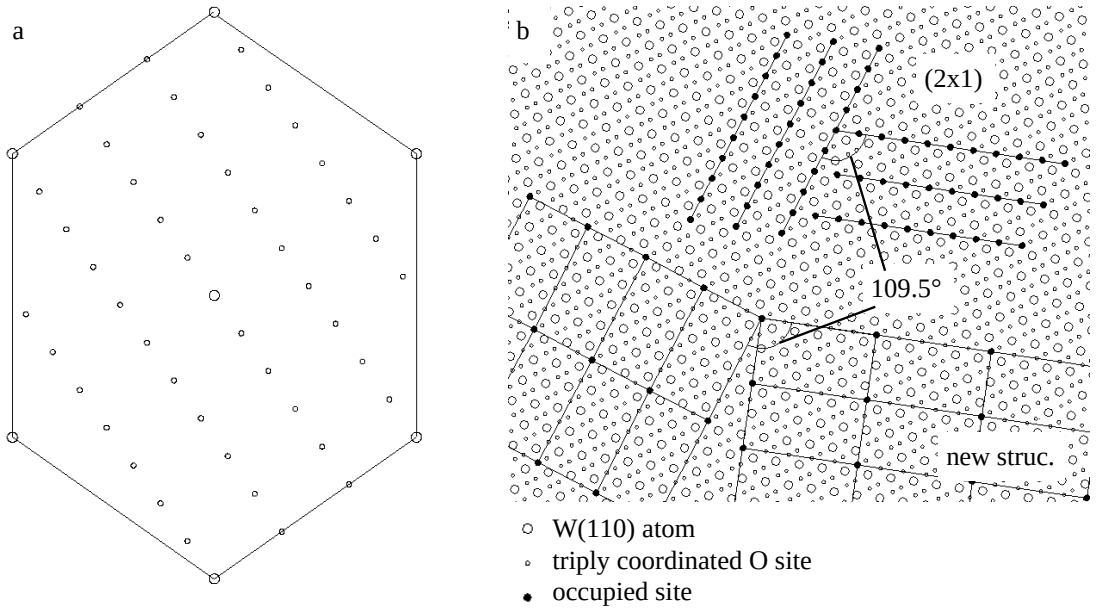

Fig. 1 (a) Diagram of the LEED intensity pattern observed for one domain of the new structure of oxygen adsorbed onto W(110). (b) The real-space model derived from (a) showing both rotational domains as well as the 2x1 structure for comparison. Note that both types of structures have rotated domains at 109.5°. The chosen oxygen adsorption sites are inferred based on the preferred triply-coordinated sites for oxygen on W(110) found in another study.[5]

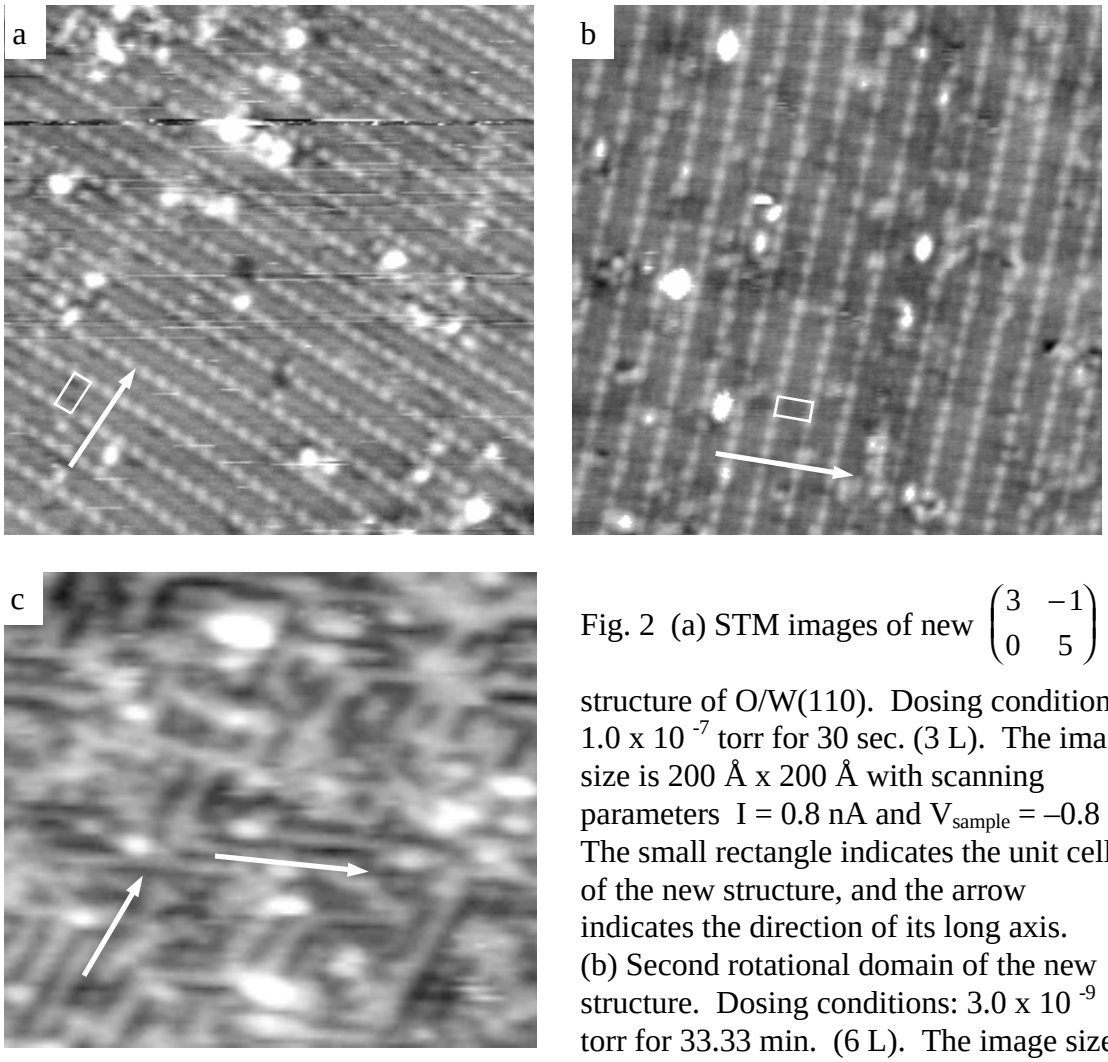

Fig. 2 (a) STM images of new $\begin{pmatrix} 3 & -1 \\ 0 & 5 \end{pmatrix}$ structure of O/W(110). Dosing conditions: 1.0 x 10^{-7} torr for 30 sec. (3 L). The image size is 200 Å x 200 Å with scanning parameters I = 0.8 nA and V_{sample} = –0.8 V. The small rectangle indicates the unit cell of the new structure, and the arrow indicates the direction of its long axis. (b) Second rotational domain of the new structure. Dosing conditions: 3.0 x 10^{-9} torr for 33.33 min. (6 L). The image size and scanning parameters are the same as in (a). The (2x1) structure in (c) was formed in another region of the same sample as in (a). Note that the arrows indicate parallel domain structures between the (2x1) structure and each of the rotated domains in (a) and (b). Image size is 88 Å x 77 Å with scanning parameters as in (a).

ANALYSIS

Based solely on the LEED pattern, the structure was determined to be $\begin{pmatrix} 3 & -1 \\ 0 & 5 \end{pmatrix}$ in matrix notation relative to the W(110) substrate.[8] As shown in the diagram in Fig. 1(b), the primitive unit cell for this structure is a perfect rectangle, 7.74 Å x 13.68 Å, and includes 15 tungsten atoms. The oxygen adsorbate atoms have been placed in one of the two equivalent triply coordinated hollow sites, which have been determined to be favored in previous studies.[5] We therefore expect 20 possible domain types: the two rotations, two possible adsorption sites, and five possible lateral positions along the long unit cell axis. From the STM images shown in Fig. 2, the unit cell was measured to be 7.3 Å by 13.3 Å, matching closely the results obtained by LEED, with an error of 5.7% and 2.7% respectively.

This new structure typically forms concurrently with the (2x1) structure in a different region of the same sample. The new structure shown in Fig. 2(a) was formed simultaneously with the (2x1) structure shown in Fig. 2(c). These two different ordered structures were found in regions 1-2 μm apart. Since the W(110) substrate is not visible in any of these STM images, we infer the unit cell orientation by comparison with the (2x1) structure in Fig. 2(c). The long side of the unit cell in Fig. 2(a) is aligned with one domain of the (2x1) structure shown in 2(c). From the known (2x1) structure, the closer-packed rows make an angle of 109.5° with the other (2x1) domain. Thus, the LEED-derived real space structure shown in Fig. 1(b) would have the same angle between the long sides of the unit cell for the two different rotational domains.

The higher resolution image shown in Fig. 3(a) shows details of the inner structure of the unit cell. The proposed structure inferred from this image is shown in Fig. 3(b), which has 6 oxygen atoms per unit cell. The long side of the unit cell appears to be bounded by rows of (3x1)—like structures, while the unit cell corner sites are unoccupied and surrounded by a rectangular array of occupied sites. The coverage derived from this structure at full saturation is then 6/15=0.40 ML.

We can compare the coverage of this new structure with that of the partially saturated (2x1) structure in Fig. 2(c), since both of these were obtained on the same sample. A software threshholding technique[9] was used to compute the partially saturated (2x1) coverage from an STM image. The oxygen adsorbate atoms were assumed to be the darker spots in the images,[10] and their coverage area was computed. Dividing this area by the total image area gives the adsorbate coverage, which was found to be 0.374 ML. Since the new structure occurs on the same sample in the same experiment, it must have the same coverage. The coverage for the new structure, as determined this way from the STM image of the (2x1) structure, thus agrees with the model coverage within 9.4%.

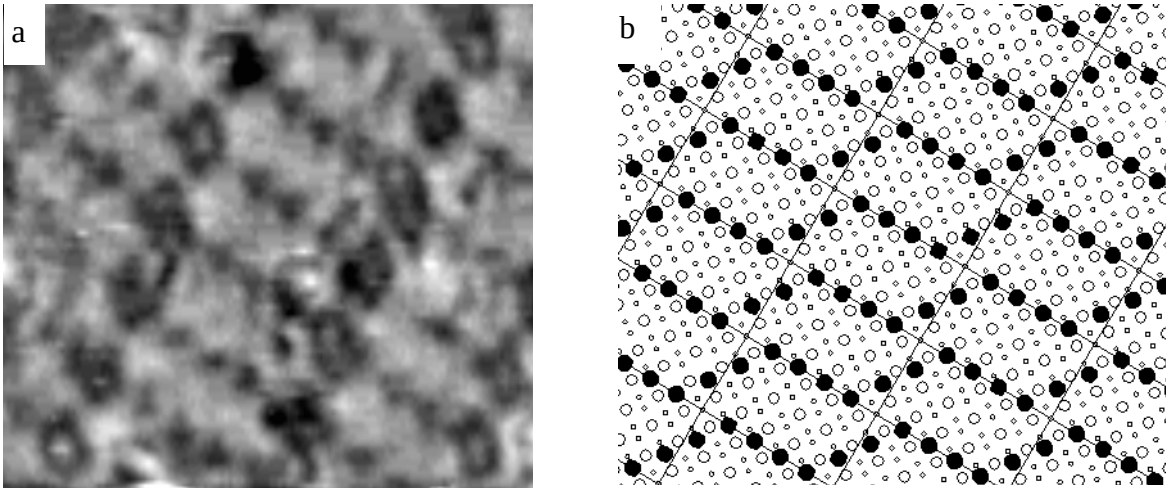

Fig. 3 (a) STM image shows details of the inner structure of the unit cell. Image size is 50 Å x 43 Å with scanning parameters I = 0.8 nA and V_{sample} = 0.8 V. (b) Proposed model for structure. Oxygen appears to form a partial 3x1 structure with unoccupied unit cell corner sites surrounded by two additional oxygen atoms. Full coverage for this structure is 0.40 monolayers. For symbol description see Fig. 1(b) legend.

CONCLUSION

In conclusion, a new ordered structure $\begin{pmatrix} 3 & -1 \\ 0 & 5 \end{pmatrix}$ was discovered by dosing oxygen on W(110) at 3 to 6 L. Both LEED and STM confirm a structure which has been seen in many different experiments and on two different W(110) crystals. This structure coexists with the (2x1) structure in different areas of the same sample. Comparison of the orientation of the new unit cell with that of the (2x1) structure and its known lattice orientation confirms the proposed structure. Based on higher resolution STM images, the location of the oxygen atoms was determined. The oxygen coverage of this model, 0.40 ML, agrees within 9.4% with the coverage computed by measuring areas of a (2x1) structure formed simultaneously on the same sample.

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