

# Adsorbate-induced reconstruction and overlayer structures of sulfur on Ir(110): An STM study

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The adsorption of sulfur on the Ir(110) surface was investigated by scanning tunnel microscopy, low energy electron diffraction (LEED), and Auger electron spectroscopy. Upon annealing to 700–1000 K, sulfur induces a missing-row reconstruction of the substrate at minimum coverages of  $0.15 \pm 0.05$  ML (Monolayer). At 0.5 ML sulfur coverage a  $p(2 \times 2)$ -2S structure with  $p2mg$  symmetry is observed, which is compatible with an earlier LEED analysis of that structure. At higher coverages up to saturation, a  $c(2 \times 4)$ -6S structure develops for which a structural model is proposed. At saturation coverage, the LEED pattern exhibits additional streaks at  $\frac{1}{4}$  positions in the  $[\bar{1}10]$  azimuth. The streaks are due to sulfur dimers in a second adsorbate layer, which can be desorbed by annealing at 1100 K. Surprisingly, the atoms in the dimers seem to be located in on-top positions over sulfur atoms of the first layer, leading to long-range order in the  $[\bar{1}10]$  direction only.

## I. INTRODUCTION

We investigated the adsorption of sulfur on the Ir(110) surface by means of scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES). The adsorption of electronegative adsorbates like sulfur on catalytically active surfaces is important both with respect to poisoning of the catalytic reactions<sup>1</sup> and with respect to adsorbate induced reconstructions.<sup>2</sup>

The structure of the clean Ir(110) surface has been characterized previously by LEED,<sup>3,4</sup> low-energy ion-scattering analysis,<sup>5,6</sup> He-atom diffraction,<sup>7</sup> and STM.<sup>8,9</sup> Whereas in the early LEED studies a  $(1 \times 2)$  missing-row model was found to agree best with the data,<sup>4</sup> the structure remained controversial until an STM study revealed the stabilization via (331) minifacets,<sup>8</sup> which was corroborated by other studies.<sup>7,9</sup> This structure is also compatible with the ion scattering experiments, where a “streaked  $(1 \times 3)$ ” LEED pattern was observed,<sup>5,6</sup> and the ion-scattering data were interpreted in terms of a  $(1 \times 3)$  missing-row model coexisting with unreconstructed  $(1 \times 1)$  patches.<sup>6</sup>

For sulfur adsorption on Ir(110) two LEED studies exist so far,<sup>10,11</sup> where a  $p(2 \times 2)$ -2S structure with  $p2mg$  symmetry was reported at 0.5 ML coverage, and a structural model on the basis of a  $I(V)$  analysis was provided.<sup>11</sup> Since sulfur was adsorbed on a  $(1 \times 2)$  reconstructed Ir(110) surface in those studies, apparently no effect on the substrate reconstruction was observed.

In the present paper we show that sulfur indeed lifts the faceted reconstruction of the substrate and induces a  $(1 \times 2)$  missing-row structure. At sulfur coverages near 0.5 ML a  $p(2 \times 2)$ -2S overlayer develops on the missing-row reconstructed surface and the STM data agree well with the model proposed in the previous LEED studies. Near saturation coverage, a  $c(2 \times 4)$  structure is observed that was already mentioned in an early LEED study, but without assigning a structural model.<sup>10</sup> Such a model is developed on the basis of the STM data.

## II. EXPERIMENT

The experiments were performed in an ultrahigh-vacuum system with a background pressure in the low  $10^{-11}$  mbar range. The sample used in the present paper was the same as the one used previously in some of the ion-scattering experiments.<sup>5</sup> It was cleaned in a separate preparation chamber by repeated cycles of 500 eV  $\text{Ar}^+$  ion bombardment (sample current approximately  $5 \mu\text{A}$ ) and subsequent annealing at 1000 K for 10–15 min. The sample was then analyzed in a different chamber by STM, LEED, and AES. The crystal was regarded as clean when no contaminations could be detected by AES, and a well-defined LEED pattern with sharp spots and low background was observed. Also in the STM no significant amounts of protrusions or depressions that may be possible contaminants could be detected. After cleaning the sample, sulfur was adsorbed at the surface at room temperature via backfilling the preparation chamber with  $\text{H}_2\text{S}$  gas at a total pressure in the  $10^{-8}$  mbar range. The surface was found to be saturated after adsorption of approximately 10 L ( $1 \text{ L} = 1.33 \times 10^{-6} \text{ mbar} \times \text{sec}$ )  $\text{H}_2\text{S}$ . Further exposure to 100 L  $\text{H}_2\text{S}$  did not increase the sulfur signal in the AE spectra. Absolute sulfur coverages are determined by comparing the respective AE signals with that of the saturated surface, which corresponds to 0.75 ML as will be shown below. Because of the good reproducibility, we believe this calibration to be exact within  $\pm 0.05$  ML.

## III. RESULTS AND DISCUSSION

An STM image of the clean surface is shown in Fig. 1, where also the corresponding ball model is depicted. Since the LEED pattern [Fig. 2(a)] consists of facet spots only, it exhibits a complex  $I(V)$  behavior when the spots move towards their respective (0,0) beams upon increasing the primary beam energy. The zero-order spots of the (331) and  $(33\bar{1})$  facets are not visible on the screen at normal incidence [normal incidence refers to the (110) plane]. At certain ener-

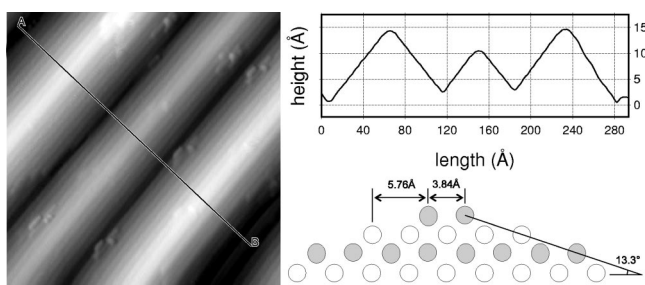


FIG. 1. (left panel) STM image of the clean, faceted Ir(110) surface,  $(250 \times 250) \text{ \AA}^2$ ,  $U_t = 0.1 \text{ V}$ ,  $I_t = 1.0 \text{ nA}$ . A section along  $[100]$  across several “grooves” is shown in the upper-right panel. The sides of the ridges are  $(331)$  facets, as depicted in the ball model (lower-right panel).

gies the pattern resembles a  $(1 \times 3)$  structure due to coincidence of the facet spots.<sup>8,9</sup>

After sulfur adsorption, no changes in the LEED pattern were observed apart from a higher background. Because of the small average size of the  $(331)$  facets, no long-range ordering detectable by LEED would be expected at this stage. Upon annealing to 700–1000 K the LEED pattern gradually converts to a well ordered  $(1 \times 2)$  structure after low-sulfur exposures of approximately 2 L [Fig. 2(b)]. Lower exposures were not sufficient for developing a well-ordered  $(1 \times 2)$  pattern. At exposures of approximately 4 L, a  $p(2 \times 2)$  pattern with characteristic beam extinctions indicative for a glide-plane symmetry is observed, as shown in Fig. 2(c). Increasing the exposure further up to saturation, the pattern changes to a  $c(2 \times 4)$  structure with slightly higher background, which can be reduced by subsequent annealing to 600–900 K [Fig. 2(d)]. After annealing, additional

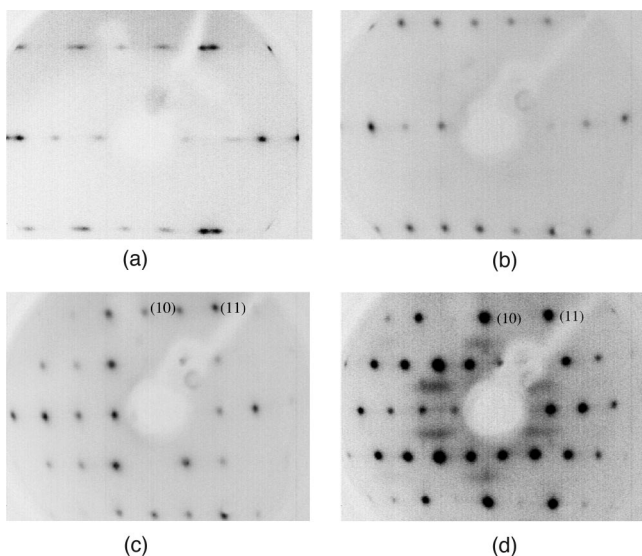


FIG. 2. LEED pattern of the Ir(110) surface. (a) Clean surface, the spot splitting is due to the superposition of beams from different facets, electron energy 90 eV. (b)  $(1 \times 2)$  pattern of the sulfur-stabilized missing-row reconstructed surface at low-sulfur coverages, electron energy 72 eV. (c)  $p(2 \times 2)$ -2S structure at 0.5 ML sulfur coverage, electron energy 75 eV. (d)  $c(2 \times 4)$ -6S structure of the sulfur saturated surface, electron energy 89 eV. The contrast is enhanced in order to show the faint streaks between the spots.

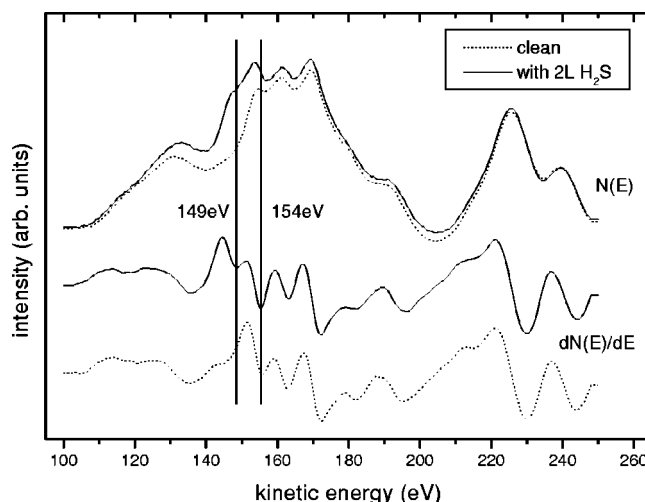


FIG. 3. AE spectra of the clean surface and after exposure to approximately 2 L  $\text{H}_2\text{S}$ . In the lower part the  $dN(E)/dE$  signal is displayed, the upper part shows the integral  $N(E)$  spectra. The spectra are smoothed using a Savitzky-Golay filter (Ref. 21) with a 4 eV window. Primary beam energy is 5 keV.

weak streaks appear in the  $[\bar{1}10]$  azimuth [indicated in Fig. 2(d)], as was previously reported.<sup>10</sup>

In Fig. 3 Auger spectra for the clean surface and after exposure to approximately 2 L  $\text{H}_2\text{S}$  are shown. The sulfur coverage is  $0.15 \pm 0.05 \text{ ML}$ , calibrated using a spectrum of the fully developed  $p(2 \times 2)$ -2S structure (see below). The shoulder on the low-energy side of the Ir(154 eV) peak and the slight increase of the Ir(154 eV) peak are indicative of sulfur adsorption. At lower coverages than shown here, sulfur may be difficult to detect. However, lower coverages were not sufficient to induce a  $(1 \times 2)$  structure, so that it is questionable, if the reported  $(1 \times 2)$  structure of Ir(110) in the past was due to sulfur contamination. Since the amount of sulfur necessary for such a restructuring is well above the sensitivity limit of AES measurements, we consider sulfur contaminations unlikely, although to our knowledge, only the very first Ir(110) study shows an AE spectrum.<sup>3</sup> In the spectrum shown in that study, clearly no S contaminations sufficient for a  $(1 \times 2)$  restructuring are present. The only possible contamination detectable in the published spectrum may be Si, which induces a  $(1 \times 2)$  reconstruction, too.<sup>12</sup> We note, however, that the authors of Ref. 3 report the presence of an imperfect  $(1 \times 2)$  structure with streaked extra spots in some of their experiments. These features can in hindsight be attributed to facet spots, indicating a reasonably clean Ir(110) surface.

Note that our AE spectra of the sulfurized surface exhibit two peaks at 149 eV and 154 eV (the latter overlaps with an Ir peak of the same energy, which can be eliminated by subtraction of a spectrum of the clean surface) which can be attributed to sulfur, whereas the S LMM peak was reported to consist of a single peak at 153 eV.<sup>13</sup> Whether this fine-structure is due to different sulfur bonding sites or due to a deexcitation of the initial sulfur core hole via the substrate valence band, as was proposed for several sulfur/metal adsorbate systems,<sup>14</sup> will be the subject of further experiments. At the present stage we see no indication for different bonding sites from our STM data.

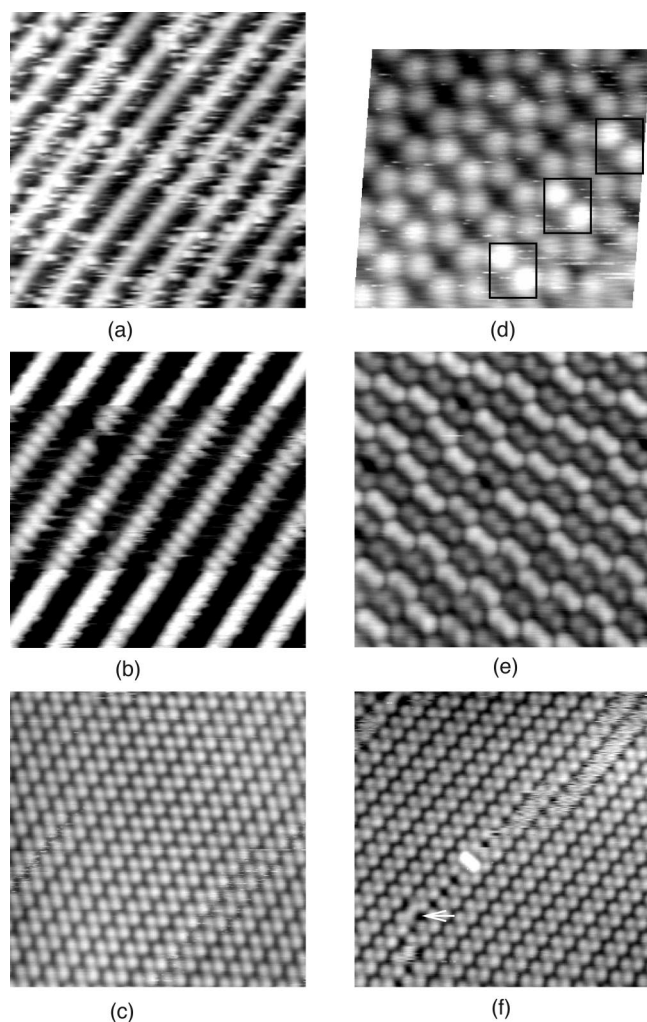


FIG. 4. STM images of the missing-row reconstructed Ir(110) surface with varying sulfur coverage. The  $[\bar{1}10]$ -direction in all images runs along the diagonal from the lower left to the upper right. (a) Noisy image, possibly due to the mobile sulfur. The sulfur atoms have not yet formed larger domains ( $65 \text{ \AA}^2$ ),  $U_t = -50 \text{ mV}$ ,  $I_t = 15 \text{ nA}$ . (b) “Clean” part of the surface with resolved missing-row structure ( $50 \text{ \AA}^2$ ),  $U_t = -20 \text{ mV}$ ,  $I_t = 15 \text{ nA}$ . (c) Fully developed  $p(2 \times 2)$ -2S structure at 0.5 ML ( $95 \text{ \AA}^2$ ),  $U_t = 900 \text{ mV}$ ,  $I_t = 1 \text{ nA}$ . (d) High-resolution image of the  $c(2 \times 4)$  structure near saturation coverage ( $37 \times 35 \text{ \AA}^2$ ),  $U_t = -900 \text{ mV}$ ,  $I_t = 0.1 \text{ nA}$ . Note the three pairs of atoms in the lower-right corner (indicated by boxes) which are brighter (higher) than the others. The height difference corresponds to approximately  $0.4 \text{ \AA}$ . (e)  $c(2 \times 4)$  structure at saturation coverage. The surface is almost completely covered by additional dimers [brighter atoms of panel (d)], which are ordered in the  $[\bar{1}10]$  direction, but long-range order in  $[001]$  is missing. ( $67 \text{ \AA}^2$ ),  $U_t = -10 \text{ mV}$ ,  $I_t = 3 \text{ nA}$ . (f) The surface of (e) after annealing at 1100 K. Most of the dimers are desorbed, only a single one is left in the middle of the image, located on a small  $c(2 \times 4)$  domain. The surrounding areas have converted back to the  $p(2 \times 2)$  structure. A position is marked where an additional sulfur atom is incorporated in the adsorbate layer. ( $100 \text{ \AA}^2$ ),  $U_t = -900 \text{ mV}$ ,  $I_t = 1 \text{ nA}$ .

Figure 4(a) shows an STM image of a terrace after adsorption of 2 L  $\text{H}_2\text{S}$  and subsequent annealing at 1000 K, and only a somewhat “noisy” missing-row structure with some additional atoms near the ridges of the  $[\bar{1}10]$  rows can be seen, which can be attributed to sulfur. This noise is not

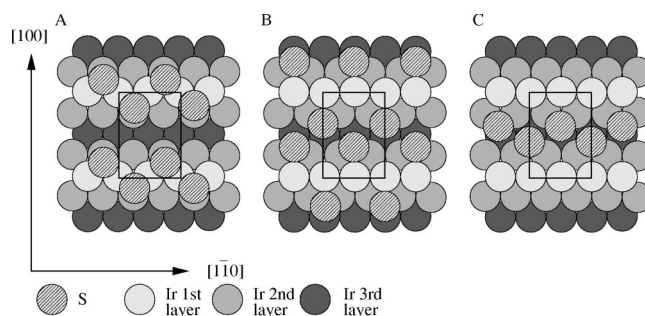


FIG. 5. Three possible models of the  $p(2 \times 2)$ -2S structure with  $p2mg$  symmetry. Model A is compatible with the STM data [compare Fig. 4(c)].

found on clean parts of the surface, where the structure of the substrate can be clearly resolved, as shown in Fig. 4(b). Obviously, the diffusion of the sulfur atoms is too fast to allow stable imaging at low coverages.

As the coverage increases, the S atoms coalesce to larger islands, and finally a fully developed  $p(2 \times 2)$  structure at 0.5 ML coverage is obtained, as shown in Fig. 4(c). The sulfur adsorbs in zig-zag rows along the  $[\bar{1}10]$  direction, with neighboring rows being in phase, so that the sulfur-sulfur distance along  $[001]$  (i.e., across the zig-zag rows) is always the same. In previous LEED studies, several models with  $p2mg$  symmetry were proposed (Fig. 5) for the  $p(2 \times 2)$  structure.<sup>10,11</sup> In addition, a model with  $p1g1$  symmetry with equal domain sizes was considered.<sup>10</sup> The latter can directly be ruled out by our STM observations, since only one domain is found in the experiments. Of the  $p2mg$  models shown in Fig. 5, model “C” can be discarded simply by measuring the lateral distances between the S atoms in images like Fig. 4(c). The width of the zig-zag rows in the  $[001]$  direction in that model is too narrow compared to the experiment. From images like Fig. 4(a) and when some sulfur atoms have already coalesced to small islands, it is seen that sulfur adsorbs near the top of the ridges of the missing-row structure, and not in the troughs between them. Furthermore, the troughs between the zig-zag rows in Fig. 4(c) are quite deep ( $0.6 \text{ \AA}$ ), which would not be expected for model “B”. Additionally, since the Ir atoms on the ridges of the missing-row structure would be exposed in the structures shown in models “B” and “C,” they should be visible in atomically resolved STM images, which is not the case. Hence, only model “A” is compatible with the STM data, in agreement with the LEED study.

The quoted arguments imply a simplistic image interpretation, in the sense that each “bump” in the STM images is attributed to an atom. For single sulfur atoms, this is predicted by theoretical calculations,<sup>15–17</sup> and is also in agreement with several previous STM studies, e.g., see Ref. 17 and 18. For dense adsorbate overlayers, however, interference effects may occur, as has been nicely demonstrated in Ref. 19. In the present experiments we have no evidence for such interference effects, since the observed contrast remains the same, regardless of overlayer structure, tunneling parameters, or the tip used. Thus we feel encouraged to apply the mentioned simple interpretation to the images presented here. We note, however, that occasionally the glide-plane symmetry was lost in some images of the  $p(2 \times 2)$  structure,



as reported for the CO/Ni(110) system.<sup>20</sup> However, since the beam extinctions in the LEED pattern clearly indicate such a symmetry, we believe this to be an artifact.

At saturation coverage a  $c(2 \times 4)$  structure is formed, accompanied by additional pairs of sulfur atoms (which we call “dimers” for simplicity) in a second adsorbate layer, as discussed in the following [Figs. 4(d) and 4(e)]. The dimers have a minimum separation of four nearest-neighbor spacings in the  $[\bar{1}10]$  direction, whereas long-range order in  $[001]$  is missing. Obviously, the dimers cause the additional streaks in the LEED pattern at  $1/4$  positions in  $[\bar{1}10]$  [Fig. 2(d)].

Figure 4(d) shows the  $c(2 \times 4)$  structure in detail. The displayed section corresponds to a part of the surface that is not completely covered by the additional dimers. In the image, only three dimers are present, indicated by boxes. It is clearly seen that the  $c(2 \times 4)$  unit mesh is formed by the same zig-zag rows as the  $p(2 \times 2)$  mesh, but now they are in antiphase. Strikingly, the atoms of the dimers differ only in their apparent height from the other sulfur atoms, whereas their lateral (in-plane) coordinates are positions of the  $c(2 \times 4)$  unit mesh. That means that they are either outward buckled sulfur atoms of the  $c(2 \times 4)$  structure, or they may be sulfur atoms in a second adsorbate layer adsorbed in an on-top position over sulfur atoms of the first adsorbate layer. The latter structure seems quite unusual, since it involves an energetically unfavorable on-top position, but experimental evidence suggests that indeed the latter model may be the correct one: First, the apparent height of the dimers is approximately  $0.4 \text{ \AA}$ , which is in good agreement with experimental findings for S/Ni(100).<sup>18</sup> The observed height difference seems quite large for a mere buckling effect, and hence may indicate a real double-layer structure. This argument is, of course, rather weak, since apparent heights in STM images are known to be determined by electronic effects, and may not necessarily scale with geometric heights. The second, and more important, argument is that the number of the dimers scales with the sulfur AE signal (although we have not tried to verify if the relation is strictly linear). In fact, the AE signal of the saturated surface, corresponding to a maximum number of dimers as in Fig. 4(e), is 1.5 times the one of the complete  $p(2 \times 2)$  structure, thus equals 0.75 ML, if attenuation effects of the AE signal are discarded [Fig. 6(a)].

Given that the dimers indeed are adsorbed in a second layer, one can assume that the binding may be weaker compared to the sulfur atoms in the first layer. Hence, the dimers may be less thermally stable, and may be desorbed by heating. This is, in fact, experimentally observed upon heating the saturated surface to approximately 1100 K.

The streaks in the LEED pattern of the  $c(2 \times 4)$  structure vanish and the pattern converts back to a  $p(2 \times 2)$ , accompanied by a decrease of the sulfur AE signal by a factor of approximately 0.67 [see Fig. 6(a)]. STM images taken after cooling to room temperature show large domains of the  $p(2 \times 2)$  structure, with only some small residual  $c(2 \times 4)$  patches that are decorated by a few dimers, as in Fig. 4(f). In the figure a single dimer is left, sitting on a local  $c(2 \times 4)$  domain. At the position indicated by the arrow, also the shift from a  $p(2 \times 2)$  to a  $c(2 \times 4)$  structure is seen on a local scale: At this position an additional sulfur atom is incorpo-

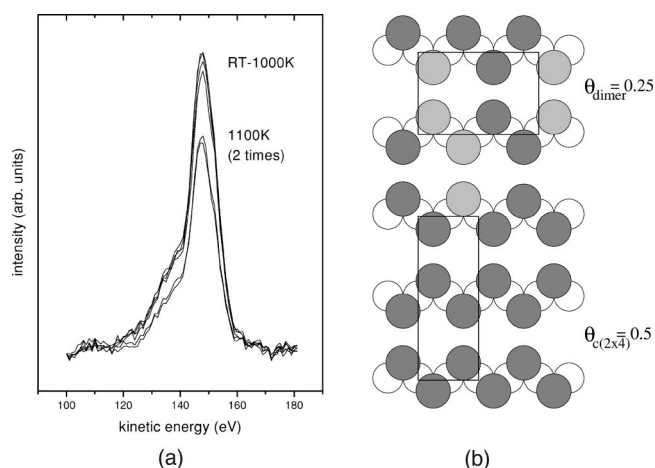


FIG. 6. (a) AE spectra  $[N(E)]$ , primary beam energy 5 keV] after heating the saturated surface to different temperatures. A spectrum of the clean surface is subtracted from each curve to yield the sulfur signal only. A significant decrease of the sulfur signal can be noticed only after annealing to 1100 K. A second anneal at 1100 K does not lead to further changes. The ratio of the area under the RT and 1100 K curves is 1.5, consistent with a coverage of 0.75 ML and 0.5 ML for the  $c(2 \times 4)$  and  $p(2 \times 2)$  structure, respectively [see panel (b)]. (b) Schematic model of the  $c(2 \times 4)$ -6S structure. Only first layer Ir atoms (white) and sulfur atoms in the first (dark grey) and second (light grey) adsorbate layer are shown. The sulfur atoms in the second adsorbate layer (dimers) contribute 0.25 ML to the coverage at saturation.

rated in the first adsorbate layer, which induces a shift of the zig-zag rows, so that they are in antiphase for the  $c(2 \times 4)$  structure. Since this leads to a closer approach of the sulfur atoms of two adjacent zig-zag rows, this structure may be considered as energetically unfavorable, which would explain why it is only observed in the presence of the dimers, which apparently act as stabilizers for the  $c(2 \times 4)$  structure.

The simple double-layer model, as shown in Fig. 6(b), is compatible with the experimental data, though it involves the unusual on-top sites for the dimer atoms. We note, however, that we never observed a *single* atom in an on-top position, so that some interaction between the dimer atoms seems to be crucial. The lack of long-range order of the dimer structures in  $[001]$  [Fig. 4(e)] is easily explained by the model, since along this direction, the available on-top positions shift by a lattice constant in  $[\bar{1}10]$ . This shift can be either in the  $[\bar{1}10]$  direction or in the  $[1\bar{1}0]$  direction, leading to more or less randomly meandering bands of dimers. Also the experimentally observed saturation coverage of 0.75 ML agrees well with the model: At saturation, the dimers contribute a maximum of 0.25 ML to the total coverage, which yields 0.75 ML together with the 0.5 ML of the first adsorbate layer.

We note that the detailed conversion mechanism between the  $p(2 \times 2)$  and the  $c(2 \times 4)$  structure cannot be revealed by the STM images shown here. Although images like Fig. 4(f) suggest that additional sulfur atoms induce a shift along the  $[\bar{1}10]$  direction, this could also be a “side effect.” A second mechanism may be that every other zig-zag row flips around the  $[\bar{1}10]$  axis along the ridges of the missing-row structure. The latter scenario would not need any mass transport in the

$[\bar{1}10]$  direction, but requires an intermediate adsorption at lower coordinated sites, e.g., a short-bridge site on the ridges. Whichever of the two possible mechanisms is energetically more favorable, should be revealed by theoretical calculations. A hint could be the noise that is always found in regions where a  $p(2\times 2)/c(2\times 4)$  conversion takes place [e.g., in Fig. 4(f), above the dimer in  $[\bar{1}10]$ ]: There is evidence that the noise is due to sulfur atoms moving between two neighboring fcc sites. This means that they apparently do not cross the ridges, i.e., the first mechanism with mass transport in the  $[\bar{1}10]$  direction would then be the correct one.

#### IV. SUMMARY

In conclusion, the adsorption of approximately  $0.15\pm 0.05$  ML sulfur on the clean Ir(110) surface lifts the faceted reconstruction of the substrate and induces a  $(1\times 2)$  missing-row reconstruction. This deconstruction is thermally activated, and is completed within a few minutes at temperatures of 1000 K. At sulfur coverages near 0.5 ML, a  $p(2\times 2)$ -2S overlayer structure with sulfur adsorbed in zig-zag rows along  $[\bar{1}10]$  is observed, in agreement with previous reports. The structural model derived by a quantitative LEED study<sup>11</sup> agrees well with the present STM data, i.e., sulfur adsorbs over an fcc site formed by two first layer atoms and one second layer atom of the substrate.

Near saturation coverage, the structure of sulfur on Ir(110) consists of zig-zag rows of sulfur similar to the  $p(2\times 2)$  structure at 0.5 ML. The difference is a shift by a nearest-neighbor distance in the  $[\bar{1}10]$  direction between two adjacent rows, so that they are in antiphase, leading to a  $c(2\times 4)$  configuration. This structure is suggested to be stabilized by sulfur dimers in a second adsorbate layer, sitting in on-top positions over first layer sulfur atoms. The fact that only pairs of sulfur atoms (the dimers) have been observed in this adsorption site, suggests that single S atoms are not stable in the on-top configuration. The dimers have a minimum spacing of four nearest-neighbor distances in the  $[\bar{1}10]$  direction and thus contribute 0.25 ML to the coverage at saturation, giving a saturation coverage of 0.75 ML. They show no long-range ordering in  $[001]$  due to the on-top position, which explains why in the  $c(2\times 4)$  LEED pattern only faint additional streaks at  $1/4$  positions in the  $[\bar{1}10]$  direction are seen. The dimers can be desorbed at temperatures higher than 1000 K. The surface then converts back to the  $p(2\times 2)$  structure. Detailed structural data provided by further experimental studies would be useful to test the proposed on-top adsorption geometry of the dimer atoms.

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