An STM, AES and LEED study of the segregated sulfur on Pd(111)

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Abstract

At elevated temperatures, 700 K, sulfur segregates to the Pd(111) surface. The coverages as measured by Auger electron spectroscopy (AES) are in the range of 0.1 to 0.25 monolayers. The LEED pattern represents a clear $(\sqrt{7} \times \sqrt{7})$ R 19.1-S° structure. With the scanning tunneling microscope (STM) the $\sqrt{7}$ structure is found on parts of the surface only. The position of the adsorbed S atoms is the fcc threefold hollow site. Beside the $\sqrt{7}$ structure, part of the surface is covered by a disordered layer of sulfur. A sizeable part of the surface is covered by sulfur in a (2×2) structure. The adsorbate in that structure is mesoscopically ordered in triangular 2D clusters with a rather narrow size distribution. The triangles contain between 15 to 66 sulfur atoms. The $\langle 110 \rangle$ edges of the Pd(111) surface are 'decorated' with sulfur, also in a (2×2) structure. These structures run parallel to the steps with a width of 4 to 5 atoms.

1. Introduction

Palladium is a well known catalyst, not surprising when noting the position of Pd in the periodic table. In the neighbourhood of Pd we find the catalysts Ni, Rh, Ag and Pt. On many of these catalysts sulfur acts as a 'poison'. In the presence of S reactions are inhibited which take place on the 'clean' catalyst. On Pd(111) sulfur plays a role in the conversion of C_2H_2, acetylene, to C_4H_4S, tiophene [1]. At a coverage of about 1/4 monolayer of S this cyclization reaction is accelerated, especially when the surface has been annealed to above 400 K. During the heating the initial $(\sqrt{3} \times \sqrt{3})$ R30° structure is changed into a $(\sqrt{7} \times \sqrt{7})$ R19.1° structure as monitored by LEED and STM. In previous LEED work on the $\sqrt{3}$ and $\sqrt{7}$ structures of S on Pd(111) the S atoms were found in the threefold fcc sites [2]. More recently the LEED data have been newly analysed and a mixed Pd–S toplayer has been proposed (Grillo et al. [2]). In both studies [1,2] S was deposited on the surface via H_2S adsorption. It is also possible to create the $\sqrt{7}$ structure by S_2 gas adsorption [3]. The authors of Ref. [3] interpret their LEED results on the $\sqrt{7}$ structure as a '2D sulfide'. All authors discuss the possible presence of a disordered phase coexisting with the $\sqrt{7}$ and the $\sqrt{3}$ structure.

There is no other published data for S on Pd(111). Other fcc(111) surfaces with S adsorption have been studied recently by STM. On Rh(111) [4], Pt(111) [5] and Cu(111) [6] the $(\sqrt{3} \times \sqrt{3})$ R30°-S structure has

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been found. On Cu(111) also the $(\sqrt{7} \times \sqrt{7})$ R19.1°-S structure exists [6]. On Al(111) an incommensurate sulfide adlayer is seen by STM [7]. The incommensurate structure causes a Moiré pattern in the STM data showing up as triangular shapes with a misorientation of a few degrees with respect to the Al substrate.

In this work we report LEED, AES and STM results on S structures produced on Pd(111).

2. Experiment and results

For the experiments we use a modified Omicron STM system. We added a LEED and AES system to the analysis chamber. The LEED system is a 're-versed' arrangement. The screen is also used for RHEED [8] in connection with a Staib 20 keV electron gun. The same gun is used also for AES in connection with a Perkin–Elmer 180° electrostatic analyser. The targets are prepared by Ar sputtering and annealing cycles in the preparation chamber until 'clean' AE-spectra are found and atomic resolution is obtained in the STM (Fig. 1). The surface shows under these conditions large terraces of the order of 1000 Å^2. The steps are rather straight along $\langle 110 \rangle$ directions. After heating the crystal to above 700 K for some minutes we find the $(\sqrt{7} \times \sqrt{7})$ R 19.1°-S LEED pattern with a clear S signal in the AES data (Fig. 2). The concentration of S as moni-
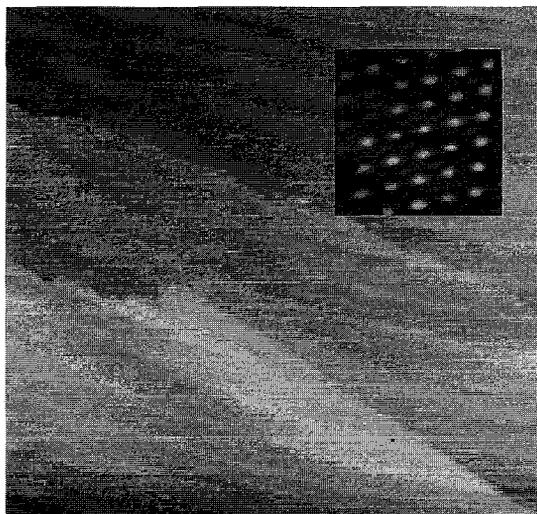

Fig. 1. 2000×2000 Å^2 STM image of Pd(111). The inset shows a 20×20 Å^2 area with atomic resolution. This gives an accurate calibration of the crystallographic directions.

tored by AES varies between 0.1 and 0.25 depending on the annealing conditions. These apparently simple LEED and AES data are accompanied by a 'zoo' of STM structures, Figs. 3a–c and 4a–c.

Fig. 3a is a survey after annealing showing the restructuring and the 'decoration' of the steps, the appearance of triangular shapes, and two types of greyish areas. Zooming into the step areas reveals a (2×2) structure on both sides of the step. The
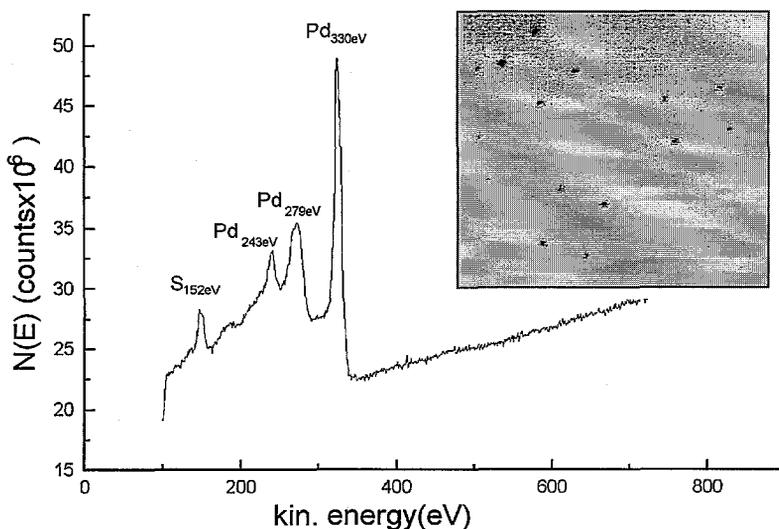

Fig. 2. $(\sqrt{7} \times \sqrt{7})$R19.1°-S LEED pattern of Pd(111) and the corresponding AE spectrum. The S concentration is 0.14 monolayers.
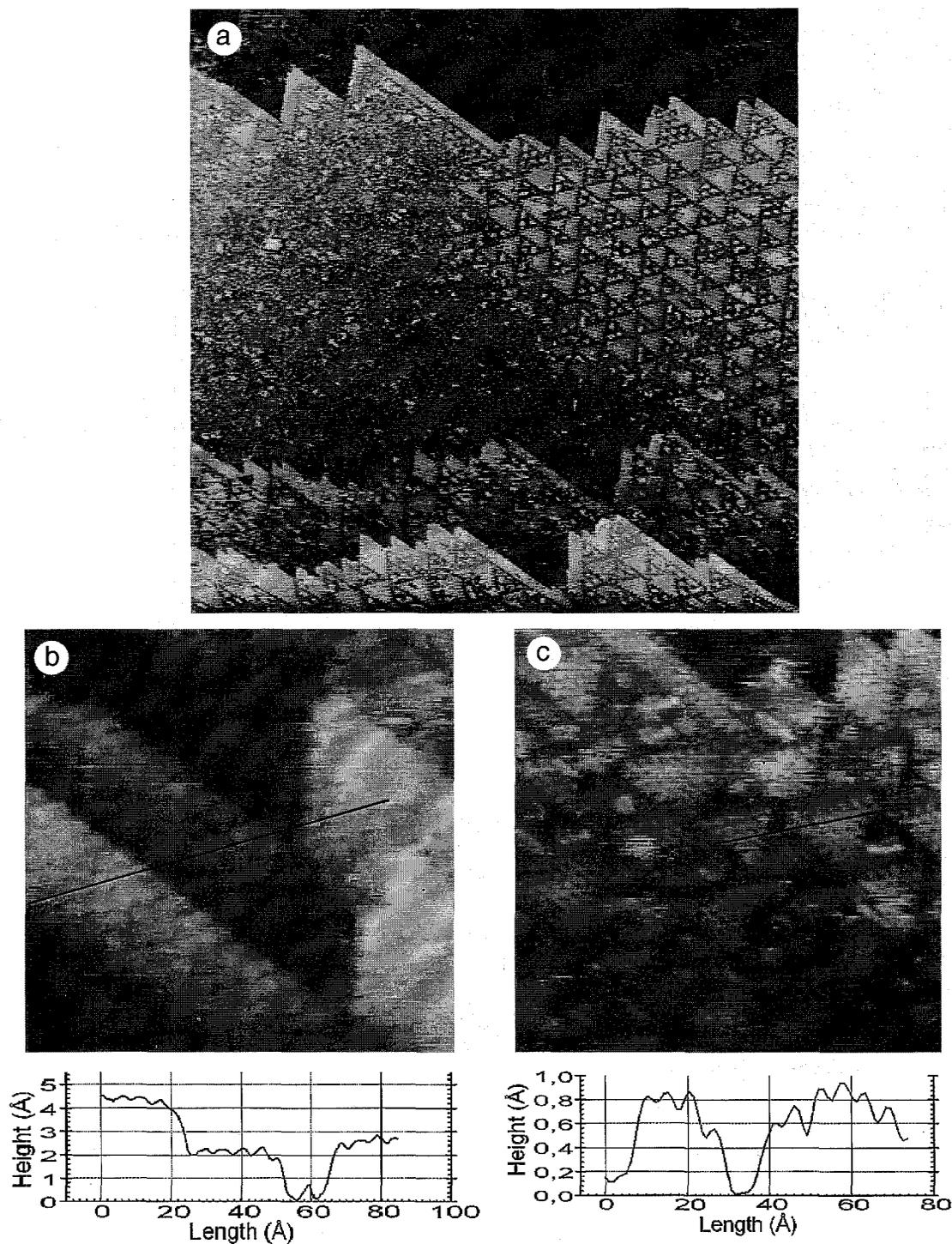
Fig. 3. (a) 2000×2000 Å^2 STM survey of the Pd(111) surface under the condition of the $\sqrt{7}$ LEED pattern. The $\sqrt{7}$ structure is found in the 'greyish' triangle free areas. (b) Zoom, 100×100 Å^2, and height scan of a step region. The structure of the 'white' or 'high' features is (2×2). The orientation is strictly parallel to the $[1\bar{1}0]$ steps. (c) Zoom, 200×200 Å^2, and height scan of the triangular shapes. The structure is (2×2) and the sides of the triangles are strictly parallel to $\langle 110 \rangle$ directions.
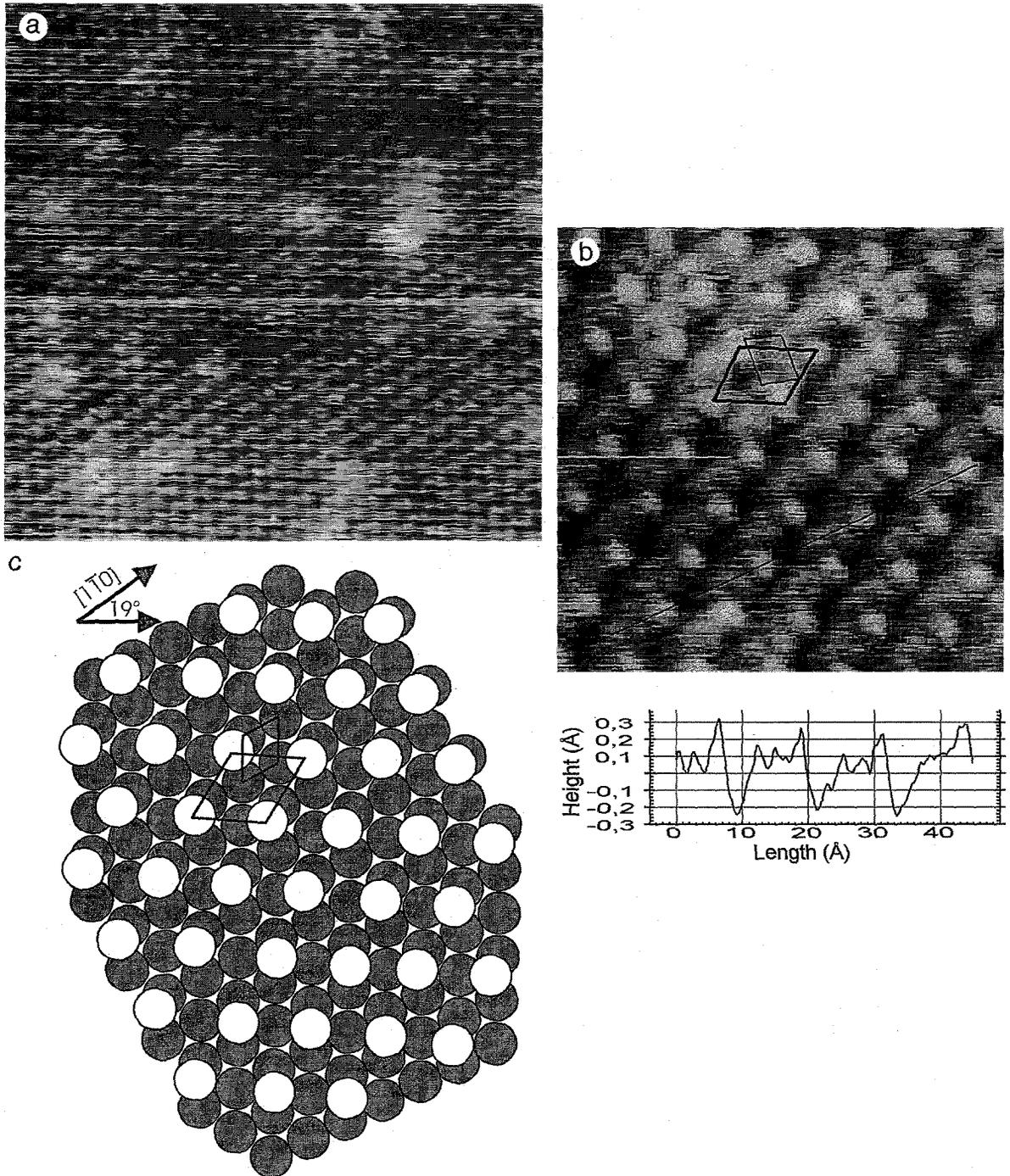
Fig. 4. (a) Large area 200×200 Å^2, view of a $(\sqrt{7} \times \sqrt{7})$R19.1°-S region. (b) Zoom, 50×50 Å^2, and height scan of the $\sqrt{7}$ structure. The black lines mark the positions of S atoms, the thin lines the positions of Pd atoms respectively. (c) Model of the $\sqrt{7}$ structure. White: S, grey: Pd. The black lines mark the positions of S atoms as in (b) and the thin lines mark the position of Pd atoms as in (b).

original step height of 2.3 Å equal to the Pd planar distance is preserved. The distance between the atoms of the (2 × 2) structure is (5.6 ± 0.5) Å. This may be compared to the atomic radius of S of 1.27 Å. This large radius makes a (1 × 1)S layer unlikely but may allow the formation of a (2 × 2) structure. Zooming into the area of triangles (Fig. 3c) we find those well aligned to the ⟨110⟩ Pd directions. The distances between the atoms of this structure is in agreement with a (2 × 2) structure, i.e. (5–6 ± 0.5) Å. The apparent height of the triangles is 0.8 Å, only compared to the height of 2.4 Å of the (2 × 2) structure formed at the step edge (Fig. 3b). The triangles have a size distribution ranging from 15 to 66 atoms per cluster, i.e. the sides of the triangles are 5 to 11 atoms long with some preference for 9 and 10. The areas between the (2 × 2) triangles show some few white spots only, like the 'disordered' areas bordering the area covered by the triangles.

Zooming now into the 'ordered' grey areas of survey scans like Fig. 3a we find the $\sqrt{7} \times \sqrt{7}$, patterns at low resolution (Fig. 4a). Zooming into smaller areas (Fig. 4b), these structures are clearly identified as the $(\sqrt{7} \times \sqrt{7})R19.1°$-S structure (Fig. 4c) reported previously [1]. However we have not only the big white spots, obviously the S adsorbate, but also the smaller spots, obviously Pd, in Fig. 4b. This allows clear identification of the S-adsorption site to be threefold fcc in agreement with the LEED analysis [2]. In the revised analysis of the 1985 LEED results, a mixed Pd–S surface layer is proposed (Grillo et al. [2]). In that structure the white spots in Fig. 4b would be Pd-atoms. At present we have no means to decide between the two possible structures. The height scans through the $\sqrt{7}$ structure show an apparent height difference between Pd and S of 0.3 Å. The Pd atoms appear at equal height. Beside the ordered phases we always find disordered areas. Longer heating seems to favour the triangular phase but we cannot report any clear correlations with the temperature or annealing time at present.

3. Discussion

The 'peak-to-peak' analysis of the AE-spectra (Fig. 2) gives an S coverage of about 0.20 monolayers. Since we find with the STM a mixture of 4 different structures, in which the 'white' or 'higher' spots are very likely S, the average coverage is not a very meaningful number. Another question raised earlier [1] is the in-depth distribution of S, i.e. it was suggested that subsurface S is present since the AES coverage is higher than necessary for the $\sqrt{7}$ structure discussed in Ref. [1]. Independent of the problem of the lateral average we looked for evidence of subsurface S following a recently developed method for quantification of AES [9]. The method is based on the concept that the shape of the AE spectra will depend not only on the chemical situation but also on the inelastic interactions of the emitted electrons with the solid. The features due to these inelastic interactions are depth dependent. Even though the analysis is at present less reliable than the equivalent method for XPS [10] it allows certainly qualitative conclusions. Applying the method to our case and assuming either the S to be on the surface or an exponential decay of the S concentration into the bulk, we find good agreement with the experiment. The latter assumption places about 25% of the S into the subsurface region. Assuming the S to form islands is not compatible with the spectral shape of the S AE-spectra, nor is the assumption that all the S is between the first and second layer. Again we have no clue whether this subsurface S is laterally or homogeneously distributed. Ion scattering experiments in a different experimental system – ex situ so to speak – shows S to segregate onto the surface [11].

In summary we have now the following new observations:
● Segregation of sulfur on Pd(111) starts at 700 K.
● The AES analysis shows up to 0.20 monolayers of S, more than 75% of which is on the surface. Hence the new features found in the STM can be identified as S.
● The segregated S changes the shape of the [1$\bar{1}$0] steps on Pd(111) from very straight to a zig-zag appearance, i.e. the average step length is shortened without a change of the average terrace size.
● At the steps S form a narrow band of (2 × 2) structures
● Near the steps large areas of triangular clusters of (2 × 2) structure in mesoscopic order are found.
● Sizeable areas of $(\sqrt{7} \times \sqrt{7})R19.1$-S are found. The S site in this structure is clearly identified as the fcc threefold hollow site.

● Sizeable areas of disordered S remain on the surface even after long heating periods.

These findings may be understood as being due to a rather week lateral S–S interaction. This is supported by the fact that e.g. the $(\sqrt{3} \times \sqrt{3})R30°$ structure survives to about 400 K only [1] and consequently is not found here.

Acknowledgements

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