

## 4 The Subsurface Oxygen

The first clear hints of subsurface oxygen formation during the CO oxidation on Pt(110) can be found in an early paper about pattern formation in catalytic surface reactions [1]. At that time, the evidence of subsurface oxygen was questioned by the objection that “probably sparsely covered areas where faceting of the Pt(110) surface might have taken place”. Two years later, the possibility of the formation of subsurface oxygen during O diffusion experiment on Pt(110) has been tentatively proposed [2]. Further investigations of O diffusion on Pt(100) brought, for the first time, conclusive experimental evidence of the presence of subsurface O [3]. Later, dedicated PEEM experiments on Pt(110) have revealed that islands of chemisorbed oxygen can be converted into subsurface oxygen, provided that CO adsorption initiates the (1 x 2) to (1 x 1) surface structure transformation on the border of the island.

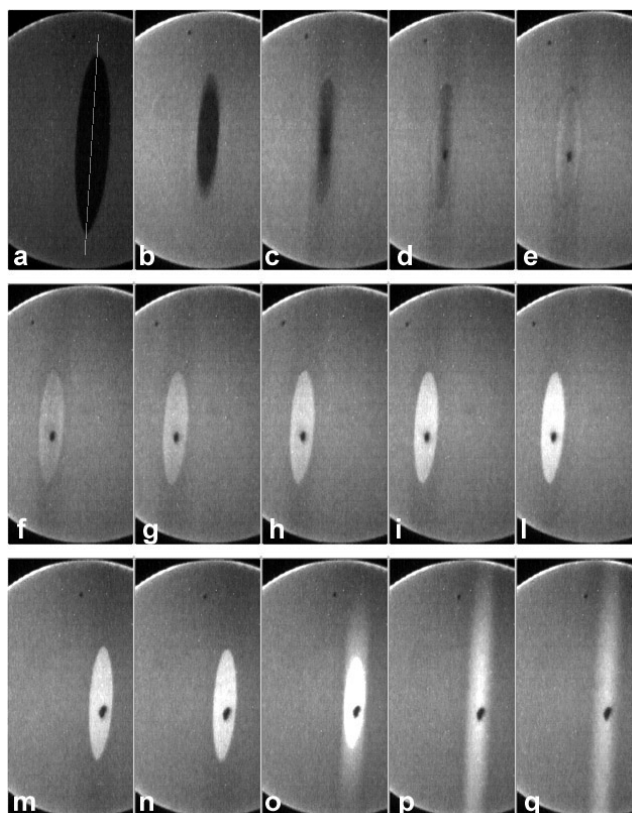


Fig. 4.1 PEEM images of the subsurface oxygen formation. Evolution of oxygen islands on a CO-precovered Pt(110) surface. Frames high: 500  $\mu\text{m}$ . a) 0 min, 320 K. b) 2 min, 443 K. c) 3 min, 483 K. d) 3 min 30s, 493 K. e) - l)  $\Delta t = 30$  s,  $T = 493$  K. m) 7 min 10 s, dosing from now on CO:  $p_{\text{CO}} = 4 \cdot 10^{-8}$  mbar. n) 7 min 20 s. o) 7 min 30 s. p) 7 min 40 s. q) 7 min 50 s.

The clean surface is first exposed to 3 L CO at 400 K, to lift the (1x1) reconstruction; thereafter the CO-covered surface is exposed to oxygen (about 50 L) at 350 K: after some time elliptical oxygen islands start slowly to nucleate from defect centers.

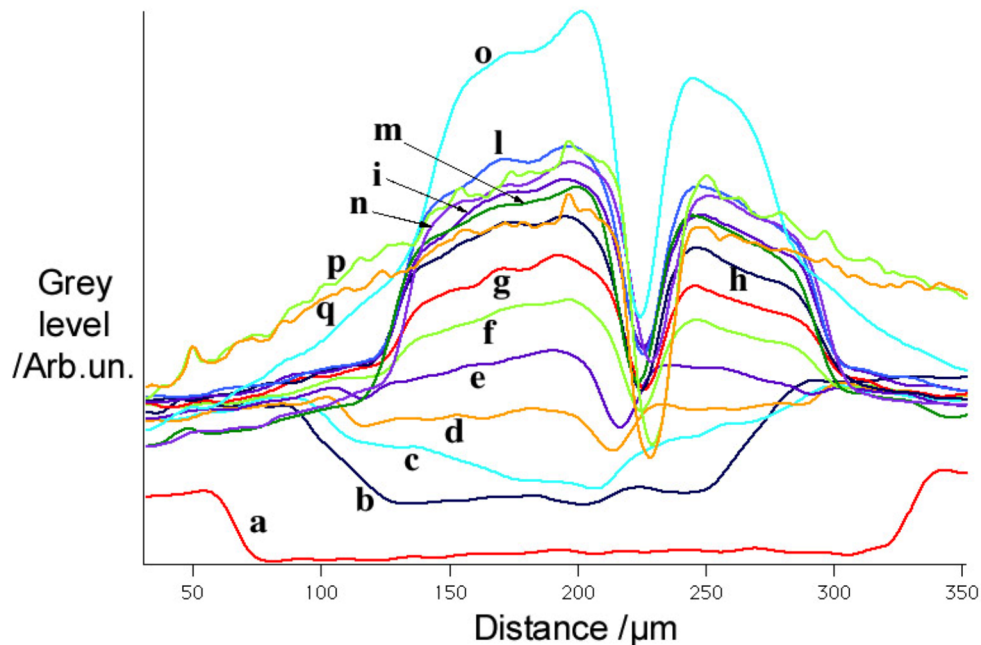


Fig. 4.2 Grey-scale plot of the section visible in the Fig. 4.1a of the corresponding frames.

As the gas supply is switched off and the sample is heated up to 500 K, the dark oxygen islands, starting from the borders, (see in Fig. 4.1 the data recorded by A. v. Oertzen and reference [4]) turn bright, much brighter than the outer region, which is supposed to be a clean Pt surface. At the same time, some one-dimensional oxygen diffusion becomes visible, as elongated shadows, in Fig. 4.1b-d. Notably, v. Oertzen and coworkers found that for larger islands the subsurface conversion always stops at about 200  $\mu\text{m}$  from the border of the island, while a surface oxygen-covered core remains unchanged even after hours.

Two hypotheses have been proposed to explain this process.

- 1) The subsurface species is created at the very moment the CO front meets the oxygen island, converting the surface species in subsurface oxygen, thanks to the surface rearrangements.
- 2) The oxygen subsurface is already present below the surface oxygen as the *normal* oxygen island grows. When the temperature is increased and the CO starts diffusing, the surface oxygen is consumed, leaving only the subsurface species; v.Oertzen and coworkers favored the first explanation.

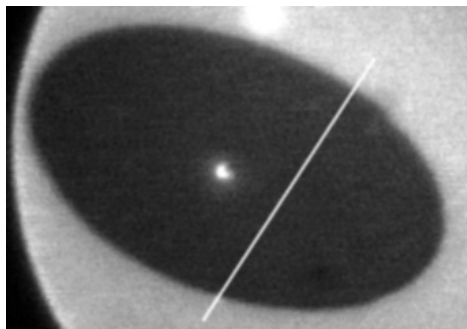


Fig. 4.2 The section of an oxygen used in the space-time diagram.

We decided to replicate the very same experiment for three reasons. First, in order to understand why the intensity of the background decreases, in contrast to the expectation of an increasingly bright surface getting clean, as the temperature approaches the CO desorption peak. Second, to compare the grayscale values of the series of images with the clean surface, eventually obtained by heating the sample up to 800 K. Third, the effects of the surface phase transition have been systematically studied by varying the temperature at which CO

has been dosed, ranging from 385 to 455 K. It has in fact been proposed that the speed of the CO-induced surface deconstruction process strongly depends on the substrate temperature.

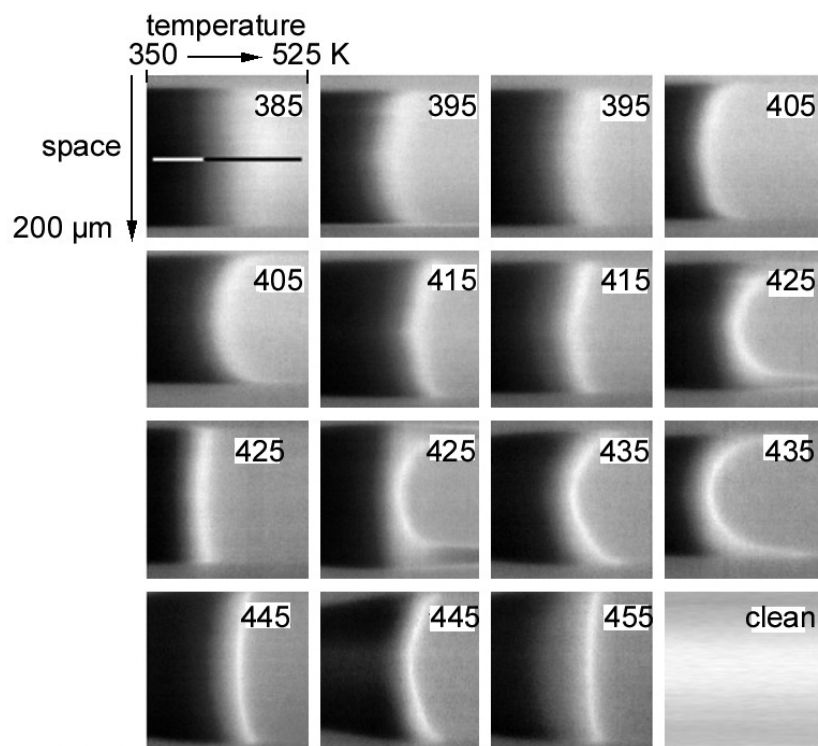


Fig. 4.3 Space-time diagrams of an oxygen island upon heating the sample up to 525 K. The temperatures of the substrate at which CO was deposited are also shown.

The time evolution of an oxygen island, grown on a precovered CO Pt(110) surface, has been recorded. A space-time diagram has then been constructed (see Fig. 4.3) by using the section shown in Fig. 4.2. In all images the original contrast has been preserved. Grayscale plots of the central section of the space-time diagram yield the curves presented in Fig. 4.4.

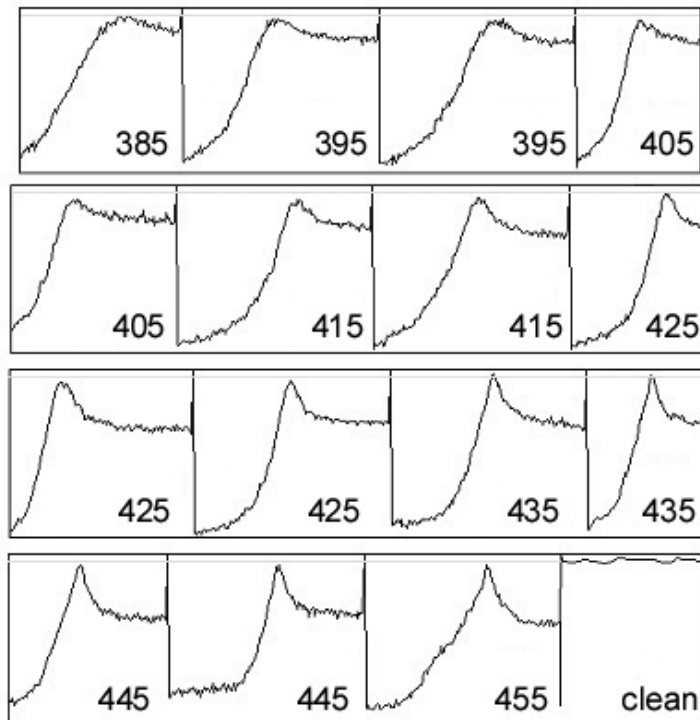


Fig. 4.4 Grayscale plots of the horizontal section of the images in Fig. 4.3.

There is a qualitative difference between the low and the high CO deposition temperature regimes. While below 415 K a fairly smooth transition is visible, above 425 K a sharp peak appears in the intensity plots. A ring-like, bright structure arises between the dark, oxygen covered and the mainly clean regions. However, here there are two main differences with the cited work of v. Oertzen. The bright areas start right on the central defect and not on the border of the island. Moreover, the rings have a lower brightness (see Fig. 4.4) than the clean surface, in contrast with the expected lowering of the work function induced by the subsurface oxygen.

In conclusion, there is experimental evidence that in the present study no subsurface oxygen formation could be detected. It remains unclear, however, why the observed clean front starts from the core rather than from the borders of the oxygen island.

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- [2] A. v. Oertzen, *Untersuchung der Diffusion von Adsorbaten mittels Photoemissions-Elektronenmikroskopie (PEEM)*, Ph.D. thesis, Freie Universität Berlin, 1993.
- [3] H. H. Rotermund, J. Lauterbach, and G. Haas, *The formation of subsurface oxygen on Pt(100)*, *Appl. Phys. A* **57**, 507 (1993).
- [4] A. v. Oertzen, A. Mikhailov, H. H. Rotermund, and G. Ertl, *Subsurface oxygen in the CO oxidation on the Pt(110): Experiments and modelling*, *J. Phys. Chem. B* **102**, 4966 (1998).

