Surface Science Letters

Iodine adlattice on Pt(100) observed by STM

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A Pt(100) single crystal annealed in a hydrogen flame and cooled in a nitrogen atmosphere containing iodine shows large atomically flat terraces separated by monoatomic steps as observed by STM. On the terraces a Pt(100) $(\sqrt{2} \times 5\sqrt{2})$R45°-I adlattice was resolved. Domain boundaries due to registry degeneracy were observed.

1. Introduction

Due to their catalytic activity Pt single crystal surfaces are difficult to handle outside of a UHV system. A well known procedure for preparing well defined air-stable Pt surfaces is annealing them in a nitrogen or argon atmosphere containing some iodine [1–3]. As temperature decreases iodine strongly adsorbs on the crystal surface and protects it from contamination. In a STM study Schardt et al. [3] showed for a Pt(111) surface that this adsorbate layer forms the same highly ordered superstructures that were known from UHV experiments. They observed Pt(111)-$(\sqrt{7} \times \sqrt{7})$ R19.1°-I and (3 × 3)-I adlattices in air as well as the $(\sqrt{7} \times \sqrt{7})$R19.1°-I at the surface immersed in HClO₄ [4]. After partial desorption of the iodine they were able to resolve in situ the $(\sqrt{3} \times \sqrt{3})$R30°-I adlattice known from ex situ LEED characterization [5], and could even image the close packed Pt(111) surface below the adsorbate layer.

For Pt(100), LEED studies [2] showed that the preparation method mentioned above yields a Pt(100)-$(\sqrt{2} \times 5\sqrt{2})$R45°-I adsorbate layer which is more densely packed than the structures achievably by dosing in UHV.

We now studied a Pt(100) surface prepared in the same way by STM, investigating the surface shape in the nanometer scale as well as the adsorbate structure at an atomic level.

2. Experimental

Our homebuilt STM is a modified version of the "Beetle type" of Besocke et al. [6,7], allowing in situ tunneling microscopy of electrode surfaces [8]. The STM circuitry was designed to run under control of a PC using the STiMage software from RHK Technology, Rochester Hills, USA.

A polished Pt(100) single crystal of 10 mm diameter, oriented to within ±15', was purchased from Kristallhandel Kelpin, Leimen (FRG). It was cleaned by repeated oxidation–reduction cycles in 1M H₂SO₄, rinsed with Millipore water and then heated in a hydrogen flame for a few minutes. The hot crystal was transferred into a flask purged with nitrogen and containing some iodine crystals. After cooling to room temperature the crystal was mounted on the STM sample holder and imaged in air with an etched Pt/Ir-tip.

3. Results and discussion

The surface appeared to be highly ordered on a large scale (fig. 1), showing atomically flat terraces of up to several hundred nanometers in size surrounded by monoatomic steps. The steps predominantly run along the (100) directions which makes the surface look somehow like an artificial microstructure. Sometimes we observed steps of

double atomic height which predominantly run along the (110) direction. Terraces enclosed by double atomic steps were always much smaller than the others and approximatly rectangular in shape (see lower right corner in fig. 1). As already suggested by Schardt [9] for the case of the Pt(111) crystal, this structure is probably produced by some kind of planar etching process of the hot crystal in the iodine vapor which stops at a certain surface temperature as the crystal cools down.

Reducing the tunnel resistance to about 1 MΩ and below – conditions like those Schardt et al. [3] used to resolve iodine on Pt(111) – we obtained the image shown in fig. 2 which correlates rather well with the expected Pt(100)-($\sqrt{2} \times 5\sqrt{2}$)-R45°-I adlattice. The structure modelled by Wieckowski et al. [2] from their LEED experiments consists of rows of iodine atoms aligned along the (100) direction, every third row sitting on top of Pt-atoms. The two rows in between are slightly offset from four-fold sites with the atoms

placed at (1/3, 1/3) relative to the nearest substrate atom (in terms of the substrate lattice constant). We would expect the STM to resolve more easily iodine atoms on top of platinum atoms than those with higher coordination. Our STM images, however, show double rows along the (100) direction separated by trenches of about 0.1 nm depth. Along the trenches a slight corrugation hardly exceeding the resolution limit of about 0.01 nm was noticed.

We therefore conclude that these images show a Pt(100)-($\sqrt{2} \times 5\sqrt{2}$)R45°-I adlattice with every third row at four-fold sites, thus appearing almost invisible to the STM. The model (fig. 3) shows that the two rows in between are offset from sitting on top of Pt atoms by (1/6, 1/6). This is essentially the structure proposed by Wieckowski et al. [2] shifted by (1/2, 1/2) lattice constants of the substrate lattice. The lattice parameters we derived from various images for the ($\sqrt{2} \times \sqrt{13}$) unit cell of the ($\sqrt{2} \times 5\sqrt{2}$) adlattice are 0.38 ±

Fig. 1. Constant current image of the iodine coated Pt(100)-surface. Scan area: 400 nm × 400 nm. Bias voltage: −140 mV (tip negative); current: 1 nA.

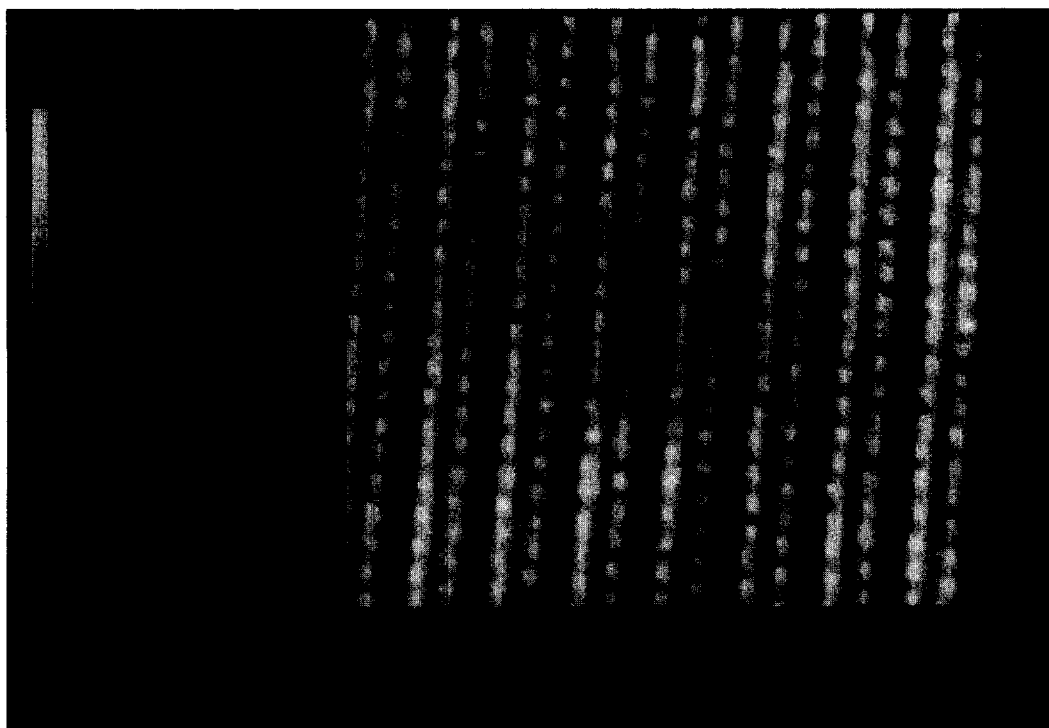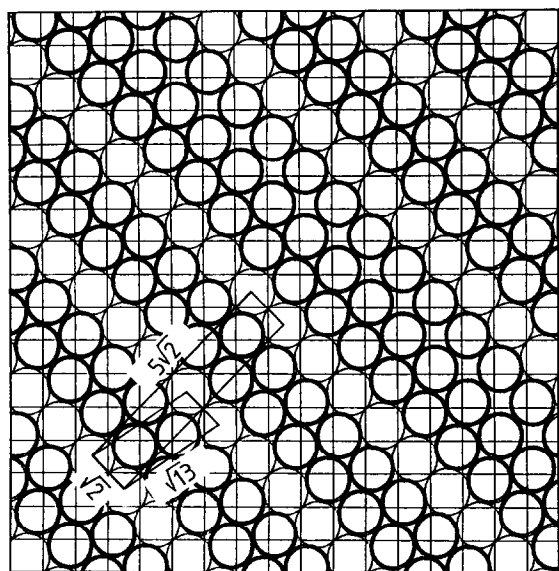Fig. 2. Same as fig. 1. Scan area: 7.8 nm × 7.9 nm. Bias voltage: −2 mV; current: 3.4 nA.

Fig. 3. Sphere model of Pt(100)-($\sqrt{2}$ × 5$\sqrt{2}$)R45°-I with an antiphase domain boundary.

0.02 nm × 0.98 ± 0.02 nm, alpha = 79 ± 3° (theoretical values 0.39 nm × 0.995 nm, alpha = 78.7°).

The distance between two adjacent rows in the image is larger than in the model structure. This means that the positions of the respective atoms are slightly shifted in the direction of the four-fold positions.

Though the structure appeared periodic over tens of nanometers we sometimes found antiphase domain boundaries due to registry degeneracy of the adlayer. Fig. 4 shows an example which we also modelled in fig. 3 as an antiphase domain boundary of two ($\sqrt{2}$ × 5$\sqrt{2}$) structures shifted against each other by (1,1) in the substrate lattice.

We always found it more difficult to get clear images at regions with broken symmetry as compared to ideally ordered regions. This might be due to an increased mobility of the adsorbate atoms near the disturbed region and the rather
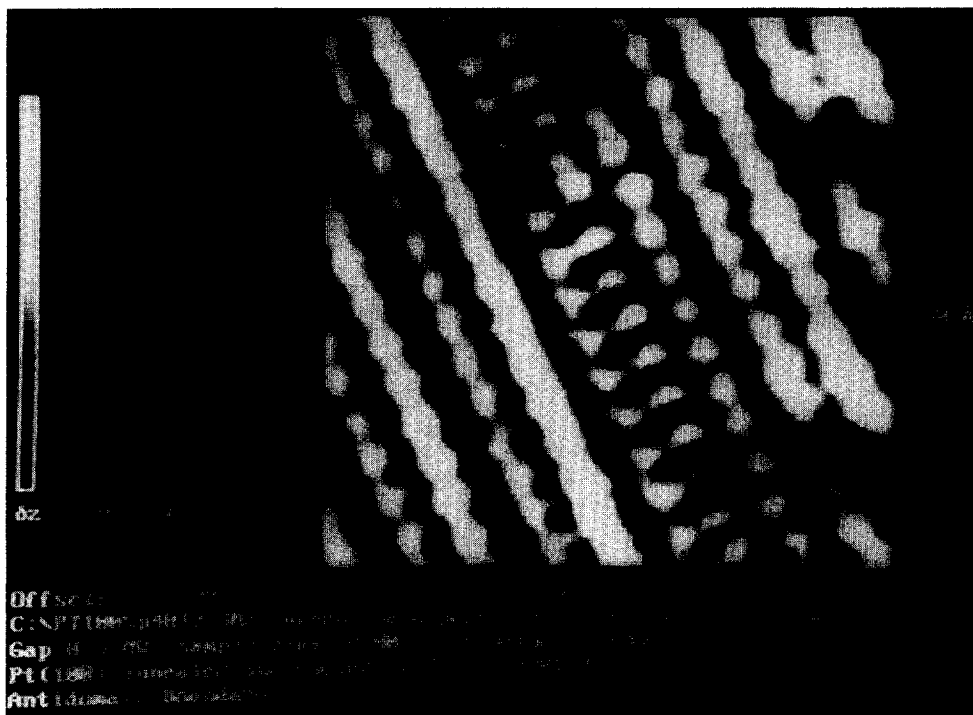
Fig. 4. Constant height image of the surface showing an antiphase domain boundary. Scan area: 5 nm × 5 nm. Bias voltage: −3 mV; current setpoint: 10 nA.

strong interaction between tip and sample we assume to have under the small gap conditions we used.

References

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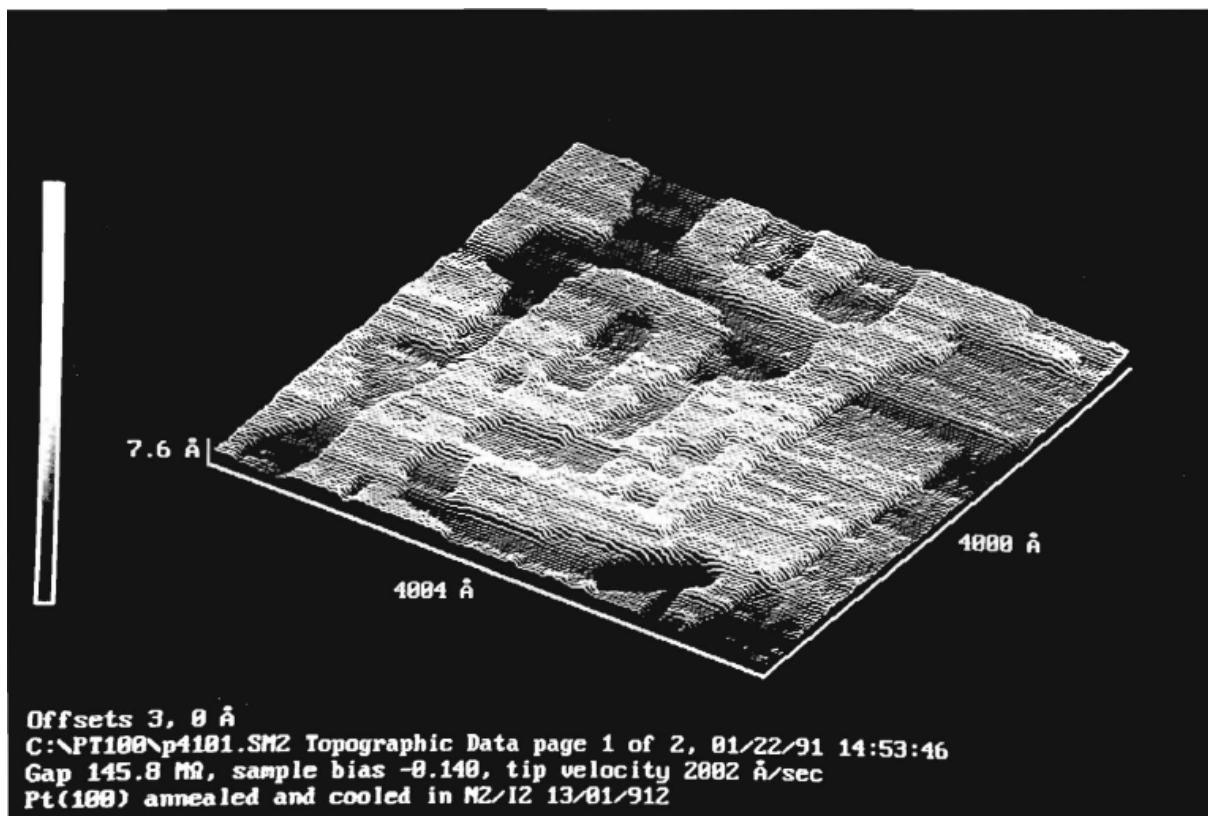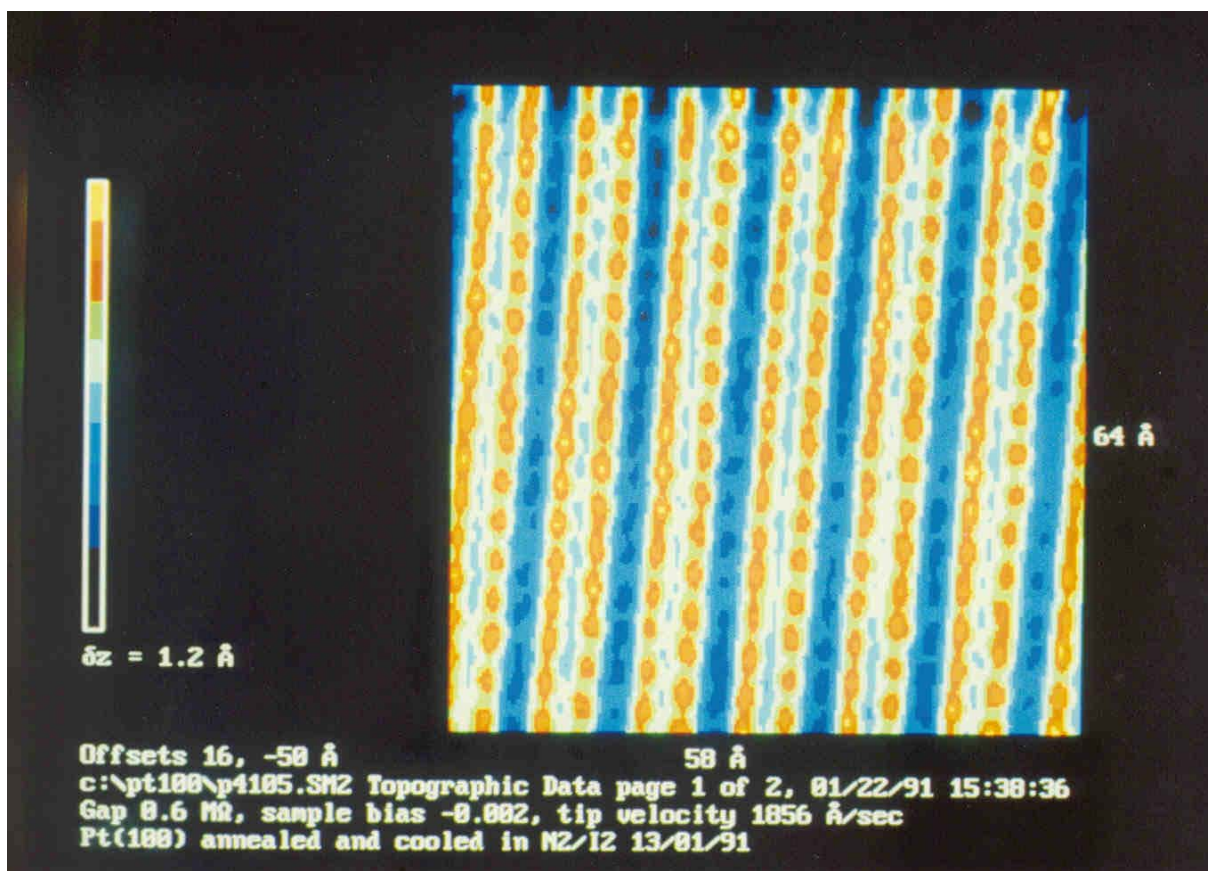[9] B.C. Schardt, private communications.

Offsets 3, 0 Å
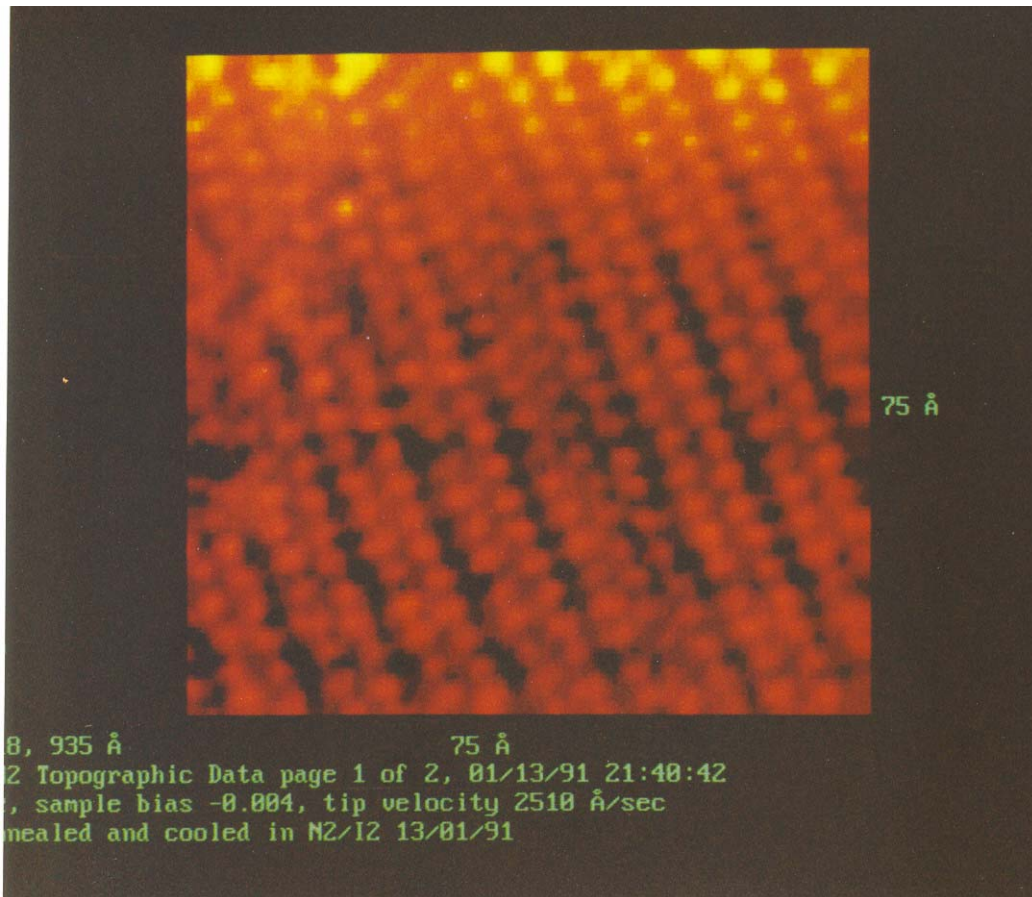C:\PT100\p4101.SM2 Topographic Data page 1 of 2, 01/22/91 14:53:46
Gap 145.8 MΩ, sample bias -0.140, tip velocity 2002 Å/sec
Pt(100) annealed and cooled in N2/I2 13/01/912

Fig.1

Offsets 16, -50 Å
c:\pt100\p4105.SM2 Topographic Data page 1 of 2, 01/22/91 15:38:36
Gap 0.6 MΩ, sample bias -0.002, tip velocity 1856 Å/sec
Pt(100) annealed and cooled in N2/I2 13/01/91

Fig.2

Fig. 4