

## INVESTIGATION OF SURFACES BY SCANNING PHOTOEMISSION MICROSCOPY

H. H. ROTERMUND, S. JAKUBITH, S. KUBALA, A. VON OERTZEN and G. ERTL

Fritz-Haber-Institut der Max-Planck-Gesellschaft,  
Faradayweg 4-6, D-1000 Berlin 33, West Germany

### Abstract

The principle of this novel technique of scanning photoemission microscopy (SPM) consists in recording the total yield of electrons emitted by UV light focussed onto a small spot on the surface through a microscope objective while the x,y-position is continuously varied. A 1x1 mm<sup>2</sup> image, for example, can be recorded within less than 10 sec with a lateral resolution of about 3  $\mu\text{m}$ . The absolute work functions of selected spots can be determined by recording the electron yield as a function of photon energy. The method is perfectly non-destructive, even with sensitive adsorbed layers. Results are shown for a polycrystalline Pt surface and its interaction with oxygen and carbon monoxide.

### 1. Introduction

Recording the total yield  $I$  of electrons emitted from a solid under the influence of light irradiation at varying photon energy  $h\nu$  is probably the most simple type of electron spectroscopy providing information on surface properties. Most conveniently the work function  $\phi$  is extracted from a plot of  $I^{1/2}$  vs  $h\nu$  (Fowler plot) [1]. Areas with differing work functions will accordingly exhibit different electron emission characteristics. If such a surface is irradiated with light within a fixed frequency range, suitable electron optics will thus provide a means for imaging the surface on the basis of its local work function differences. This is the principle underlying the photoemission electron microscope (PEEM) which was technically realized several times over the past years [2].

Spatial resolution (of the order of 1  $\mu\text{m}$ ) may alternately be achieved by focussing the light beam onto a small spot from which simply all emitted electrons are collected while scanning the position of irradiation. This is the principle of the recently developed scanning photoemission microscope (SPM) [3] which exhibits several unique

features:

- (i) By rapidly scanning the position of the irradiated spot in two dimensions, an image from a macroscopic surface area ( $\geq 1 \text{ mm}^2$ ) can be constructed with a resolution of a few microns within about 1 min (or even shorter).
- (ii) One-dimensional line scans over 1 mm can be performed within 1 sec, so that also fairly rapid processes may be followed.
- (iii) By varying the photon energy at fixed positions the absolute work functions of selected spots can be determined and may serve as quantitative fingerprint of the state of the surface
- (iv) Due to the small photon energies and fluxes the method is absolutely non-destructive, even for sensitive adsorbed phases.

In the following we shall at first briefly describe this method which has been further improved with respect to its first version. Then its capability for characterizing polycrystalline surfaces as well as of their chemical reactivity will be illustrated by means of a few examples.

## 2. Experimental set-up

The experimental arrangement is reproduced schematically in fig. 1. Inside a UHV

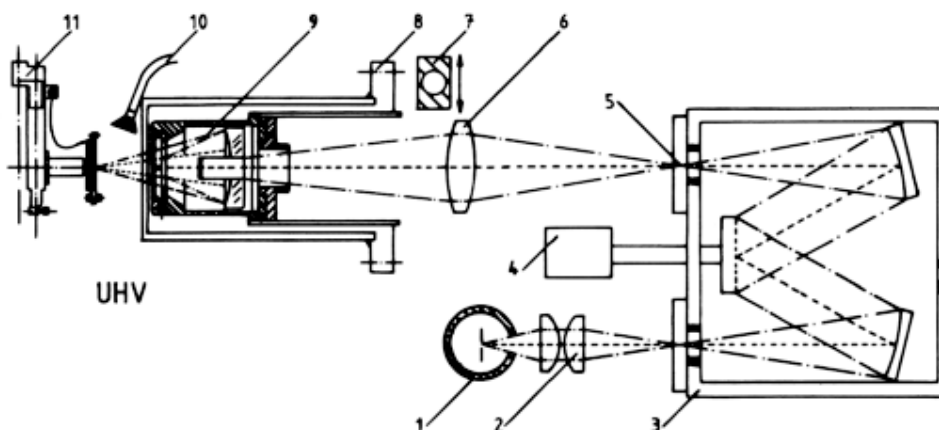


Fig. 1: Experimental arrangement for SPM:

- 1: UV light source (deuterium lamp, 0.5 mm  $\varnothing$  aperture); 2: condenser;
- 3: high intensity monochromator,  $f$  2.6, grating 600  $\text{\AA}/\text{mm}$ , 200 nm blaze;
- 4: computer controlled stepping motor; 5: variable aperture 0.1-0.6 mm;
- 6: UV-grade, quartz lens  $f = 126 \text{ nm}$ ; 7: mirror with ocular (10x) for optical adjustment;
- 8: UHV window, UV-grade quartz; 9: microscope objective;
- 10: channeltron; 11: sample holder.

system (base pressure  $3 \times 10^{-11}$  mbar) the sample is mounted on a commercial manipulator. The light from a deuterium lamp, covering the spectral region between 3 and 7 eV photon energy, passes through a monochromator and is focussed onto the sample surface by means of the objective of a Schwarzschild-type reflection microscope (Ealing X15). The sample is at a distance of 20 mm from the quartz window through which the light passes into the UHV system. The emitted electrons are collected by a channeltron (Valvo X719 BL).

As can be seen from the block diagram of fig. 2, the electronic signal from the channeltron passes first through an amplifier, from where it is either fed into a rate meter serving a chart recorder or through a gated amplifier into a counter on the computer. The latter also controls the sample position as well as the monochromator setting.

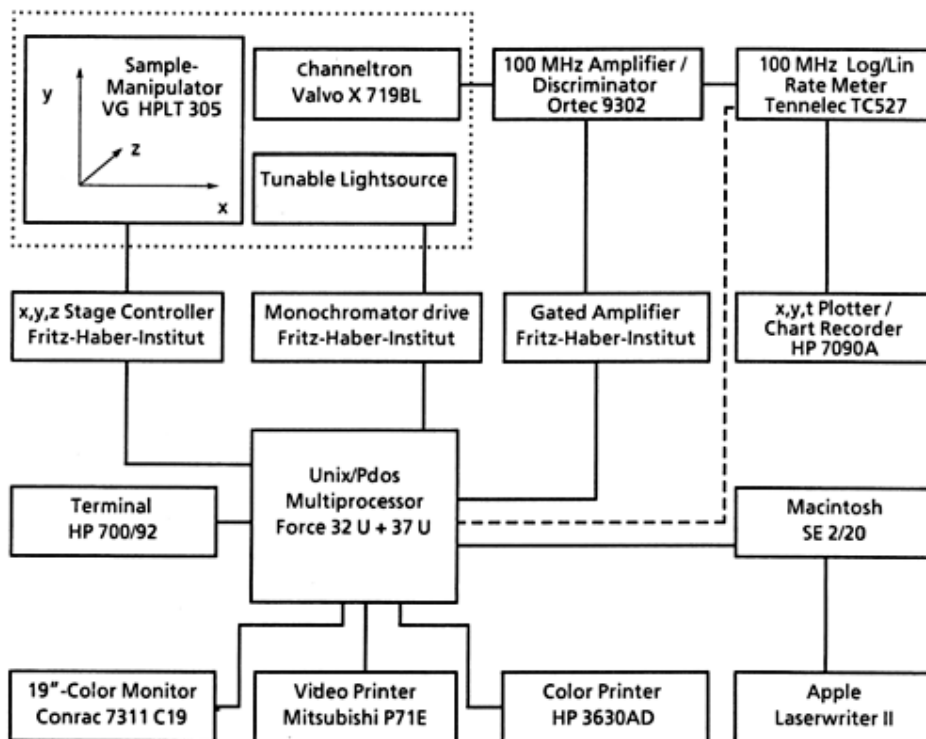


Fig. 2: Block diagram of the control and data acquisition system.

At fixed position of the irradiated spot, data for the electron yield  $I$  vs photon energy  $h\nu$  providing the local work function  $\phi$  can be taken in about 10 sec. Laterally resolved images, on the other hand, are obtained by keeping the photon energy fixed and by varying the location of the irradiated spot on the surface. This is achieved by stepping

motors (mounted outside the UHV system) in increments of  $0.5 \mu\text{m}$  per step. A third motor device varies the z-distance for optimizing the focus. The electron yield as a function of x, y may be either reproduced in terms of a grey scale or in the form of perspective 3D plots. Note that within a given SPM image the grey scale varies always from black (lowest emission intensity) to white (highest intensity) so that only within a specific SPM image intensities may be compared with each other. Alternately, line scans can be made in which the intensity is recorded only as function of one coordinate. The spatial resolution is at present about  $3 \mu\text{m}$ ; it could in principle be improved by better mechanical stabilization, while the resolution limit is about  $0.5 \mu\text{m}$ . Recording a 2D image from a  $1 \times 1 \text{ mm}^2$  area takes typically about 40 sec; with some loss in lateral resolution this period may even be reduced to about 5 sec. A line scan over 1 mm can be recorded in less than 1 sec; this mode of operation is therefore favorable for monitoring fairly rapid surface processes.

### 3. Results

Fig. 3 shows an image from a large ( $3.8 \times 4.4 \text{ mm}^2$ ) area of a clean, polycrystalline

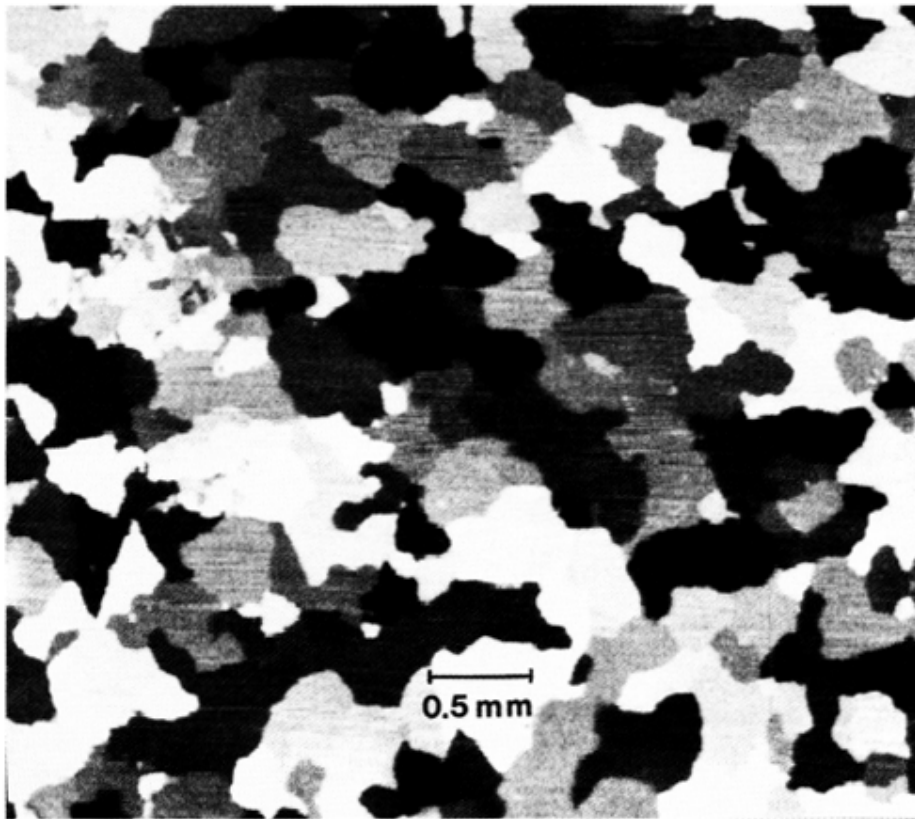


Fig. 3: SPM image from a  $3.8 \times 4.4 \text{ mm}^2$ , clean polycrystalline Pt surface.

Pt surface. The grey scale was (as also in the subsequent examples) adjusted in a way to reach from the lowest (black) to the highest (white) electron yield, which in the present case varied between  $2 \times 10^3$  and  $14 \times 10^3$  cps. This image was recorded with light exhibiting maximum intensity at  $h\nu = 6.0$  eV. The varying electron yields are due to the differing crystallographic orientations and hence work functions of the grains in the polycrystalline sample. An enlarged image from a polycrystalline Pt surface is reproduced in fig. 4a. Intensities from different spots were recorded as a function of

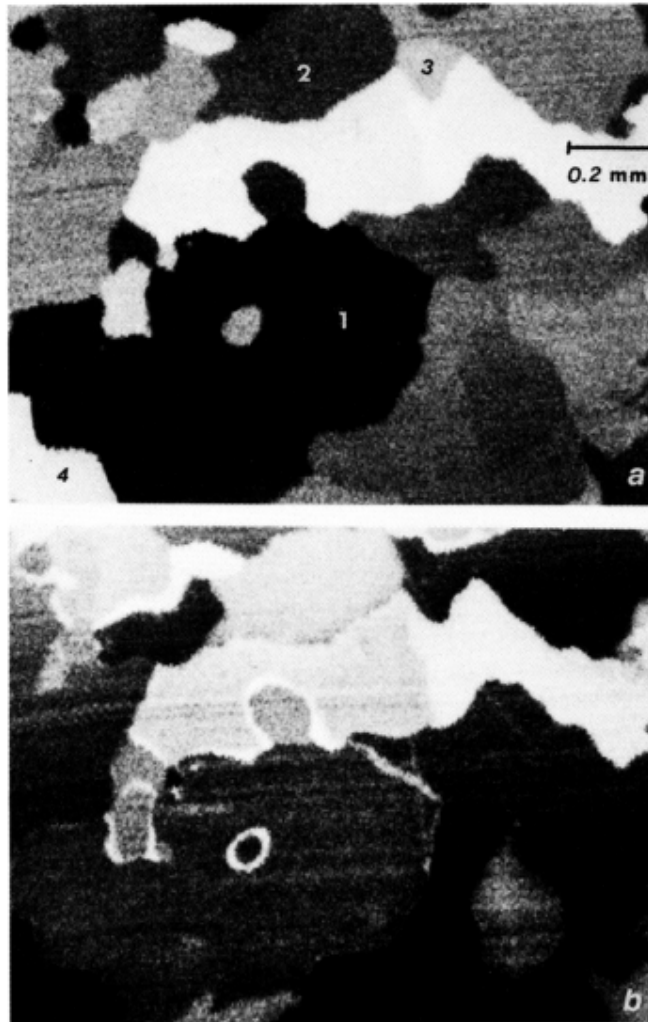


Fig. 4:SPM image from a  $1 \times 1.5$  mm<sup>2</sup> polycrystalline Pt sample a) Clean surface: plots of electron intensity vs. photon energy for marked spots are displayed in fig. 5; b) The same area after exposure to 4 L O<sub>2</sub> at 300 K.

photon energy. A representative set of data (for those spots which are marked in fig. 4a) is reproduced in fig. 5 in the form of so-called Fowler plots,  $I^{1/2}$  vs.  $h\nu$ . Extrapolation of the straight line portion of such a plot to the abscissa yields the respective work function  $\phi$ . In the present case values ranging from  $\phi = 5.72$  to 5.94 eV result. Analysis

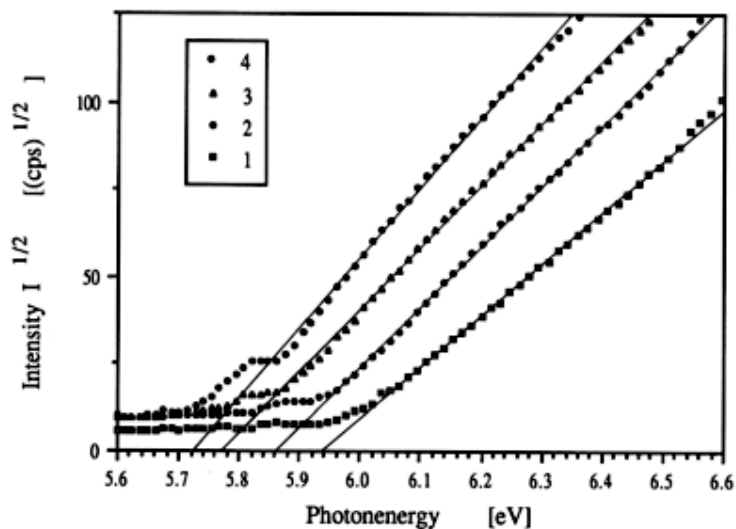


Fig. 5: Fowler plots,  $I^{1/2}$  versus  $h\nu$ , for the spots marked in fig. 4a.

of the data from a large number of patches on this polycrystalline Pt surface demonstrated that by far most of the values can be grouped into one of the three following categories  $\phi = 5.70$  eV, 5.85 eV, or 5.95 eV. In the literature the following values for clean Pt single crystal surfaces are found: Pt(111): 5.93 eV [4], Pt(100) = 5.84 eV [4], Pt(110) = 5.67 eV [5]. It is therefore quite obvious that our polycrystalline Pt surface consists predominantly of grains with the three low-index plane orientations (111), (100), and (110).

The work function is, of course, sensitively affected by gas adsorption. This becomes qualitatively evident from a comparison of figs. 4a and b. The latter shows the same section of the surface after exposure to 4 L O<sub>2</sub> at 300 K (1 L = 1.3 × 10<sup>-6</sup> mbar s). The relative degrees of brightness have changed considerably, signaling the varying reactivities as well as dipole moments of the adsorbate of different regions. Remarkably, several of the grain boundary zones in fig. 4b appear relatively brighter than the rest of the adjacent crystallites. Since oxygen adsorption increases the work function and hence decreases the electron yield, this might indicate a lower oxygen sticking coefficient in these regions. This somewhat surprising qualitative conclusion requires, however, further detailed investigations.

Fig. 6 shows a series of images from the same section as with fig. 4, however now as perspective display, demonstrating the effect of progressing oxygen adsorption.

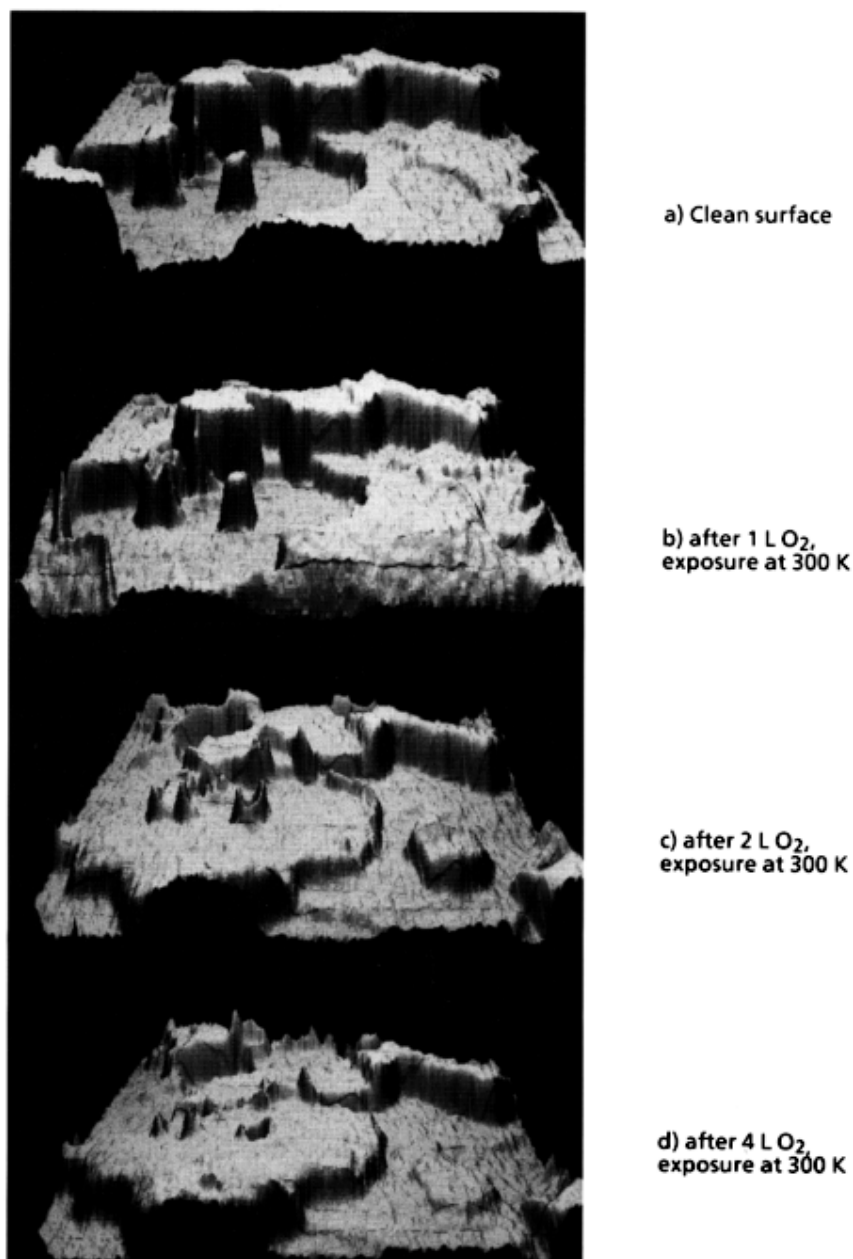


Fig. 6: Perspective representation of the intensity (z-axis) as a function of x,y-position of the same 1x1.5 mm<sup>2</sup> surface as with fig. 4.

Following the prescription given by Lange et al. [8] the best fit values for  $n$  were determined and were found to range from 2.1 to 2.7. The resulting data show that the work function of Pt(100) increases by 0.2 eV upon CO adsorption and by 0.5 eV upon oxygen adsorption, in reasonable agreement with data determined previously by means of the vibrating condenser method [7].

In summary, this novel method offers a convenient means for non-destructive imaging (with a few microns resolution) of surfaces as well of their attack by adsorption from the gas phase, whereby quantitative information can be obtained through determination of the (local) work function. First results on temporal evolution of spatial patterns studied in this manner are being published elsewhere [9].

#### LITERATURE

- 1 H. Simon and R. Suhrmann, "Der lichtelektrische Effekt und seine Anwendungen", 2nd ed., Springer, Heidelberg, 1958.
- 2 a) H. Bethge and M. Klaua, *Ultramicroscopy* **11** (1983) 207;  
b) M. Mundschau, E. Bauer and W. Swiech, *Surf. Sci.* **203** (1988) 412;  
c) M. E. Kordesch, W. Engel, E. Zeitler and A. M. Bradshaw, *J. Phys. B* (in press).
- 3 H. H. Rotermund, G. Ertl and W. Sesselmann, *Surf. Sci.* (in press).
- 4 B. E. Nieuwenhuys and W. M. H. Sachtler, *Surf. Sci.* **34** (1973) 317.
- 5 W. Sander, Thesis Fritz-Haber-Institut, in preparation.
- 6 H. O. Peitgen and D. Saupe (eds.), "Fractal Images", Springer-Verlag (1988).
- 7 R. Imbihl, M. P. Cox and G. Ertl, *J. Chem. Phys.* **84** (1986) 3519.
- 8 P. Lange, D. Grider, H. Neff, J. K. Sass and R. Unwin, *Surf. Sci.* **118** (1982) L257.
- 9 H. H. Rotermund, S. Jakubith, A. von Oertzen and G. Ert., *J. Chem. Phys.* (in press).