Recent Studies by Scanning Tunneling Microscopy

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Crystal surfaces are the seat of many interesting phenomena of both a fundamental and a more applied nature, *e.g.* heterogeneous catalysis and microelectronics, and a detailed understanding of the atomic structure of the surface can be of the utmost importance. Investigation of topographic and electronic surface structures with a local resolution on an atomic scale remained a vision until the discovery of the scanning tunneling microscope (STM).

The STM has already led to unprecedented insight, not only in several problems in surface science, but also in such areas as materials science and biology. In the present paper, we shall discuss recent experimental results in a number of different areas and thereby hope to illustrate the great versatility of the STM.

In a STM a sharp metal tip is brought so close (≈ 0.5-1 nm) to a surface, that the electrons' wavefunctions in the tip and the sample overlap. Electrons can then tunnel from the tip to the surface and vice versa, depending on the polarity of the external bias voltage ($\leq 3 V$) applied across the junction. The tunneling current depends exponentially on the width of the tunneling gap, and changing the gap by 0.1 nm can alter the current by as much as a factor of ten. The sample-to-tip distance is therefore reflected very sensitively by the magnitude of the tunneling current. The apex atom of the tip tends to dominate in the electron transfer process, resulting in atomic resolution. When the tip is raster-scanned across the surface the

Klaus Mortensen is working towards his Ph.D. A graduate in physics from the University of Aarhus, he is interested in STM studies of the surfaces of semiconductors. tunnel current can be maintained constant via a feedback circuit which applies a correction voltage to a piezoelectric drive in the vertical direction, causing the tip to retract from (or approach) the surface as the tunneling current increases (or decreases). This correction voltage can be manipulated to portray a map of the surface topography.

The geometric and electronic structures of surfaces are closely related, but using the STM one can measure the local electron density of states separately. This is done by opening the feedback loop for a fixed time, ramping the bias voltage from e.g. -2 V to +2 V and measuring the change in tunnel current as function of the applied bias voltage. This I(V) spectroscopy can be per-



Fig. 1 — Constant-current STM topographs of a Si(111) 7×7 surface of a 15 × 15 nm² region. (a) Clean Si, $I_t = 1$ nA, $V_t = -0.8$ V; (b) and (c) reacted with hydrogen to an estimated coverage of 0.1 ML: images take at the same position as (a) but with $I_t = 1.6$ nA, $V_t = -1.1$ V, and $I_t = 1.5$ nA, $V_t =$ -2.5 V respectively. The **same** 7×7 unit cell is outlined in (b) and (c). The grey scale represents a corrugation of approx. 0.2 nm in all images; surface protrusions are white, while depressions are black. A negative tip bias implies that electrons are tunneling from a filled tip to empty surface states. formed at each point of the topographic scan, thus presenting us with the marvellous opportunity of studying the surface electronic structure atom by atom.

Applications under UHV

The STM was originally developed for the study of surfaces under clean, well controlled conditions under ultra-high vacuum (UHV). The structure of the surface layer will often differ from that of the bulk crystal: either it is simply strained or it adopts a completely rearranged or reconstructed bonding configuration.

Semiconductor surfaces

Investigations of the surfaces of semiconductors represent the most active area of application of the STM under UHV conditions. A famous example is the Si(111) surface where a superlattice exists that is seven times larger in each lateral direction than the corresponding lattice for a bulk-terminated surface. Despite considerable effort using a number of different surface sensitive techniques, it was the direct imaging capability of the STM that first resolved the detailed structure of the Si (7×7) surface [1]. The generally accepted Dimer-Adatom-Stacking-fault model contains a stacking fault of the upper



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layer in one half of the 7×7 unit cell, dimer bonds along the edges of the resulting triangular subunits, and finally 12 Si atoms (denoted adatoms) in the top layer. Numerous studies of both clean and adsorbate-covered surfaces have followed since then. For example, the versatility of the STM in studying the chemical reactivity of surfaces has been demonstrated in investigations of the reaction of ammonia with silicon surfaces [2].

The reaction of the Si(111) 7×7 surface with atomic hydrogen is another example where we have used scanning tunneling microscopy and spectroscopy to give us invaluable new insight. This system has been investigated extensively for more than a decade and the generally accepted view is that the hydrogen atoms bind to the dangling bonds of the silicon surface.

The constant-current topographs of Fig. 1 illustrate the effect of a short exposure of the Si(111) 7×7 surface to atomic hydrogen. The reacted surface shown in Fig. 1b has an estimated coverage of 0.1 ML (monolayers), and on comparing this with an image of a clean surface (Fig. 1a), the apparent disappearance of a number of Si adatoms



Fig. 2 — STM topograph of a highly hydrogen reacted Si(111) 7×7 surface of a 7 × 7 nm² region: a 7×7 unit cell is outlined ($I_t =$ 2 nA, $V_t = +2.1$ V).

Fig. 3 — (a) Atomically resolved STM image of a 2 × 2 nm² region of a bare (1×1) Cu(110) surface recorded with $V_t = -0.53$ V and $I_t = 2.5$ nA. (b) STM image (7 × 7 nm²) showing the formation of "added rows" after exposure with ≈ 1 L of oxygen. (c) STM image of the Cu(110)-(2×1)O reconstructed phase at an oxygen exposure of ≈ 10 L recorded with $V_t \approx -0.8$ V and $I_t \approx 0.8$ nA. The [001] direction coincides with the y-axis in all cases.

is immediately observed. However, the topographs in Fig. 1 contain a mixture of local electronic and geometric information, so the disappearance does not imply removal (*i.e.* desorption) of Si atoms. In fact, by increasing the tunneling bias to above 2 V (independent of the polarity), most of the missing Si atoms reappear (Fig. 1c).

This dependence on the bias voltage can easily be understood in terms of hydrogen induced changes in the local electronic structure. At the low biases (Figs. 1a and 1b), the tunneling is almost completely into dangling-bond related electron states. However, if hydrogen adsorbs at the dangling-bond this state is quenched and one will instead observe a hole in the topographs. For the higher biases, states related to the back-bonds of the Si adatoms contribute significantly to the tunneling current, making it less sensitive to the possible disappearance of the danglingbond state. The disappearance of Si adatoms in Fig. 1b is thus caused by binding of hydrogen to the danglingbonds of the surface. This can be confirmed by performing local tunneling spectroscopy.

While at low coverages the hydrogen was found to bind to the existing dangling-bonds of the surface, the topograph in Fig. 2 immediately shows dramatic changes in the nature of the surface layer for higher coverages. The 7×7 symmetry is still observed, as expected from low-energy electron diffraction (LEED) measurements, but while 12 Si atoms were observed in each unit cell for the clean 7×7 surface, 42 Si atoms are now seen. This is accounted for by removal of the upper 12 Si atoms — the adatom layer — uncovering the next Si layer while preserving the stacking fault of one half of the 7×7 unit cell, as can be seen from Fig. 2. At higher exposures to hydrogen the removal of Si atoms is therefore unambiguous and the surface can accept high coverages (saturation is at ≈ 1.25 ML of hydrogen). A similar removal of the Si adatom layer has been reported recently for adsorption of chlorine on the same Si(111) 7×7 surface [3].

Such studies may shed new light on the hydrogenation of semiconductor materials, which is of technological importance because of the potential use of hydrogen to reduce the densities of deep levels in both crystalline and amorphous silicon.

Metal surfaces

Studies on metal surfaces imaged under UHV are much more scarce, probably because the relatively shallow topographic variations require the STM to have higher lateral and vertical resolutions for atomic imaging; and because metal surfaces are more reactive and thus more difficult to deal with experimentally. Very recently, new and interesting results have appeared in studies by the Fritz-Haber group [4] and by our group of dynamic processes on metal surfaces caused by adsorbate induced reconstructions.

One example is the oxygen induced reconstruction on Cu(110) which has been studied extensively in the past. It is known that molecular oxygen chemisorbs dissociatively on Cu(110), and that LEED patterns show a (2×1) structure at an oxygen coverage of 0.5 ML. The half- and integer-order spots of the patterns are of comparable intensity, indicating a surface reconstruction. However, after more than 20 years of research, the detailed atomic structure of this Cu(110)-(2×1)O surface is still open for debate. The two structural models suggested in the past for the (2×1) reconstructed phase are the "missing row" model, where every second [001] row on the surface is absent, and the "buckled row" model, where every second [001] row is shifted outward.



Fig. 4 — STM images of the surface of an X-ray mirror (24 nm gold layer evaporated on dip-lacquered aluminum) taken at different areas from the same spot: (a) $0.1 \times 0.1 \ \mu m^2$, (b) $0.2 \times 0.2 \ \mu m^2$ and (c) $0.8 \times 0.8 \ \mu m^2$.

Fig. 3 shows a series of STM images of the surface for increasing oxygen exposure. Atomic resolution in an STM image of the clean Cu(110) surface was achieved for the first time (Fig. 3a). The formation of "added" rows of atoms (interpreted as O-Cu chains) along the [001] direction is initiated when the surface is exposed to oxygen at $\approx 100 \, ^{\circ}\text{C}$ for exposures ranging from 0.1 to 1 Langmuir (1 L = $1.34 \ 10^{-4}$ Pa.s). The shortest O-Cu chains appear to be ≈ 6 \times 0.36 nm, long indicating that there is a critical minimum length. At higher exposures (\approx 1-2 L) resulting in an O coverage of 0.1-0.2 ML, the "added" rows are found in islands developing a unit mesh, with a periodicity that is doubled in the [110] direction (Fig. 3b). Typical dimensions for these islands are 10-20 nm in the [001] direction and 1.5-2.0 nm in the [110] direction corresponding to preferential growth in the [001] direction. This structure is consistent with the observation of streaky (2×1) LEED patterns for low oxygen exposures, indicating a lack of order in the [110] direction.

Exposures to \approx 10 L bring about an O coverage of \approx 0.5 ML where most of the surface is covered with the reconstructed phase. However, several types of defects or irregularities may be observed and Fig. 3c shows some examples. There is a reconstructed terrace (A) one atomic layer below the top layer, a single chain of atoms (B) between two reconstructed anti-phase domains shifted away from the nearest neighbor chain by an extra [110] (2×1) lattice parameter, a point defect (C) that has developed from a vacancy, and a region (D) between in-phase reconstructed areas which shows a very weak corrugation with a periodicity consistent with a $c(6 \times 2)$ reconstruction.

Growth of the reconstructed phase has been studied by imaging a region of two terraces separated by a monoatomic step. The Cu(110) surface was first dosed with 1 L of O2 at 100 °C to form small reconstructed islands of Cu-O chains. Images taken while the crystal was then exposed to oxygen at room temperature and at a pressure of 1 \times 10⁻⁸ mbar show that Cu atoms were removed exclusively from the step edge of the upper terrace between the existing reconstructed (2×1) islands, and that the rate of removal differed at various points along the terrace edge. Simultaneous growth of the reconstructed islands on the lower terrace, preferentially along the [001] direction, was observed. From this, and from the observed high mobilities of both single and groups of Cu-O chains, one can conclude that the reconstructed "added" row phase grows on top of the terraces by the condensation of Cu atoms diffusing from step edges and of O atoms diffusing on the surface. The "added" row model is identical to the previously adopted "missing row" model at the saturation coverage of 0.5 ML, but the two models differ significantly in terms of mass transport.

This and a similar study of the CO induced $1 \times 2 \rightarrow 1 \times 1$ structural transformation of the Pt(110) surface [5] demonstrate the great applicability of high resolution scanning tunneling microscopy to studies of the dynamics of the nucleation and growth of adsorbate induced structural transformations.



Fig. 5 — A 30 \times 30 nm² topograph of a Si(111) surface after 'writing' the letter 'H'.

Applications in Air

It may seem surprising that the scanning tunneling microscope works as well in air or even some liquids as in an UHV. The reason is the small ($\approx 10^{-2}$ at ambient air pressure) number of atoms in the 1 nm³ volume between the tip and the sample, so one can in a sense still speak of "vacuum" tunneling.

One area where the STM may have important impact in the future is surface metrology or, more specifically, in measuring microroughness on a scale unattainable with other more conventional instruments *e.g.* a stylus profiler.

Fig. 4 shows STM images taken in our laboratory of different areas of X-ray mirrors made by evaporating gold (thickness 24 nm) on a dip-lacquered 0.3 mm aluminium foil. These mirrors are prototypes made by the Danish Space Research Institute in connection with the construction of two highthroughput X-ray telescopes to be launched into space in 1993. The topography of Fig. 4a is characterized by a few islands 2-3 nm high with a spacing in the 20-50 nm range, while in Fig. 4c a homogeneous and isotropic distribution of these characteristic features is observed. The average lateral length of the roughness was found to be $\approx 0.04 \,\mu\text{m}$, while the root mean squared value of the height variation was $R_{\rm rms} = 0.8 \pm$ 0.1 nm. From measurements of R_{rms} for mirrors with different gold film thicknesses, it was established that R_{rms} attained a minimum for a gold thickness between 8 or 24 nm. The result can be used as a guide when selecting the best coating process in the production of the X-ray mirrors.

Lithography

Another very interesting area of application of STM is lithography on a nanometer scale. Fig. 5 shows an example of 'dots' made reproducibly by applying a voltage pulse of 8-10 V to the sample when the probe tip was positioned at the desired points. This technique may have significant implications in the future for the creation of a memory media



Fig. 6 — STM imaged of a slightly curved fragment of an unstained DNA polymer (scanned area: $90 \times 90 \text{ nm}^2$). The image alternates between a repeating structure and a broad depression, identified as the major groove. The right-handed rotational sense of the helical structure is indicated with an arrow. The 4× magnified insert reveals the bipartite structure, tentatively associated with the minor groove.

with extremely high densities and storage capacities.

The fabrication of atomic-scale components and devices using STM is illustrated by the recently observation of the tunnel-diode effect on an atomic scale at Si(111) surfaces with a very high subsurface concentration of boron. The observed current-voltage characteristics were related to the presence or absence of the boron dopants at individual atomic sites (size $\approx 0.5 \text{ nm}^2$) [6].

Biological Materials

It has recently been the goal of several research groups to apply the superior resolving power of the STM to biomaterials. Unfortunately however, biomaterials are in general poor conductors, are easily deformed or damaged, and since they must usually be deposited on a conducting surface at low concentration, they are hard to find.

Fig. 6 shows a recent high-resolution image of unstained, air-dried DNA fragments (≤ 500 base pairs) deposited on a freshly cleaved, highly oriented pyrolytic graphite substrate. The observed structure is believed to be DNA preserved in the B conformation structure for the following reasons: The DNA polymer alternates between a repeating structure and a broad depression, identified as the major groove. The helical structure has a right-handed rotational sense, it repeats at regular intervals of 3.8 ± 0.6 nm, has a width of 2.5-3.0 nm and a height 1.6-1.8 nm, all in good agreement with the expectation for random sequence DNA. In the high-resolution image, each helical repeating structure appears bipartite with a narrow depression on top, which tentatively can be interpreted as the minor groove since the width of the structure is 1.5 \pm 0.1 nm, close to the expected width for the minor groove in B-DNA [7].

Concluding Remarks

The STM is a fascinating new instrument, capable of exploring the atomic scale realm. Its development from being a complicated, home-made research instrument to a fairly low-cost commercial product will diversify the applications of the instrument tremendously. New areas of application are being developed continuously: for example, it is possible to study electrode surfaces during electrochemical reactions taking place in an electrolytic cell [8]. Finally, the development of the atomic force microscope, which is capable of imaging nonconducting surfaces, will have a significant impact on the study of biological, polymeric and other materials of these types.

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Günther Harbeke

Günther Harbeke died unexpectedly in November 1989 in Zürich of a heart attack while playing tennis at the age of 60. Harbeke was born in Bippen, Germany, on 10 April 1929. He received his undergraduate and graduate education at the Technical University of Braunschweig, where he stayed on as a postdoc in the Semiconductor Laboratory of the PTB. In 1961, Harbeke moved to the RCA Laboratories in Zürich and soon became Group Head for materials research — a position which he held until his premature death. In this position he received three times the Oustanding Achievement Award. He spent sabbatical years at the RCA Laboratories in Princeton, N.J. and at the Max-Planck-Institut FKF in Stuttgart. Günther Harbeke also undertook an academic career starting at the University of Hamburg as a lecturer (1968-1970). He later became an honorary professor at the University of Köln. He was close to crowning his love for Italy, as he was recently called to the new chair of Materials Science at the University of Pavia. Harbeke was the director of two courses of the International School of Materials Science and Technology at Erice, Sicily.

Harbeke dedicated most of his research to the electronic and magnetic properties of materials. He made important and original contributions in many fields, documented by more than one hundred publications, which provided him with a world-wide reputation. Much of his early work and the stateof-the-art in his field is found in the monograph *Optical Properties and Band Structure of Semiconductors* that he wrote with D.L. Greenaway.

Günther Harbeke, however, was not only a first-class scientist and teacher, but also a strenuous supporter of our Society since 1971, when he was elected IOM delegate to the EPS Council. From 1973 to 1975, and again from 1986 to 1989 he was a respected member of the Editorial Board of Europhysics News. From 1975 until his death he made an invaluable contribution to the activities of the Condensed Matter Division, first as its Board Secretary, then as the Chairman of the Semiconductor and Insulator Section, and finally as a co-opted member and representative of CMD in the European Materials Research Society and as an Editor of the European Who's Who in Condensed Matter Physics. His premature death represents a great loss for EPS. Even more we mourn the loss of a wonderful human being, whom we shall remember and praise for his warm friendliness and optimistic attitude, his respectful fairness with colleagues and students, his tactful ability in handling delicate affairs, and his dedication to his beloved wife Ruth and children.

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