Atomic description of elementary surface processes: diffusion and dynamics

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Abstract

A large fraction of processes which are at the foundation of our technological society involve physical and chemical properties of surfaces. Catalytic reactions and semiconductor devices production are two of the most important ones.

This paper describes a sample of some of the most relevant surface science experiments which have been recently performed, in order to understand elementary surface processes of model catalytic reactions and in semiconductor technology at the atomic level. The focus is on experiments performed with scanning tunneling microscopy and atomic force microscopy which have represented, in some cases, real breakthroughs in our understanding of these phenomena.

We then present an overview of possible experimental technique developments that can be foreseen for the future and that may give us a more in-depth understanding of the elementary processes which form the basis of important complex surface phenomena. Finally, some of the challenging tasks that lie ahead for surface scientists and the collateral opportunities are discussed. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The last few atomic layers of a solid constitute its interface with the environment; on this interface a great number of molecular and atomic processes continuously take place in a quasi two-dimensional (2D) world.

These processes form the basis of some of the most important technologies on which our modern society rests for its prosperity and economic development. Information technology and telecommunications would not have been possible without the progress in device fabrication, which has required profound knowledge of semiconductor surface technology.

Most of the modern industrial chemical production is based on catalytic reactions which are just sequences of elementary processes, taking place on the surface of a suitable catalyst. Every year, more than 150 million tons of ammonia are

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produced through a catalytic process; most of this chemical is converted into much needed fertilizers for an increasingly hungry world.

In environmental chemistry, catalytic processes are of vital importance for breaking down pollutants such as automotive exhausts and industrial emissions.

The atomic/molecular surface processes play also a key role in other economically important phenomena like corrosion, metal embrittlement, friction and lubrication, just to name a few.

The interest in deepening our understanding of the phenomena which take place at surfaces is therefore very strong. A more profound knowledge holds the promise of optimizing the production rate and the selectivity of a catalyst or the physical properties and size of semiconductor devices and could be the key for mastering other promising technologies, like hydrogen storage and fuel cell development.

2. Surface structure and elementary surface phenomena

The ensemble of surface phenomena taking place at the interface between a solid and a gas phase shows usually a bewildering complexity. For this reason surface scientists have mainly confined themselves so far to the study of the well characterized surfaces which result from cutting or cleaving a mono-crystalline sample along one of the planes with lowest Miller indices. In studying a single crystal surface, one tries to obtain a suitable sample on which to conduct experiments, with a well known geometry and with a definite chemical identity.

Fig. 1a shows a picture of a clean (1 1 1) surface of aluminum as determined by scanning tunneling microscopy(e) (STM) [1]. Even though the atoms in the last plane are not exactly located in the position one would expect by an ideal "cut" through a (1 1 1) plane of an aluminum crystal (they are relaxed inwardly by a few % of the lattice parameter), still the picture may leave the impression that a surface is a well behaved sort of checkerboard: just a simple playground for the foreign atoms and molecules we may want to de-
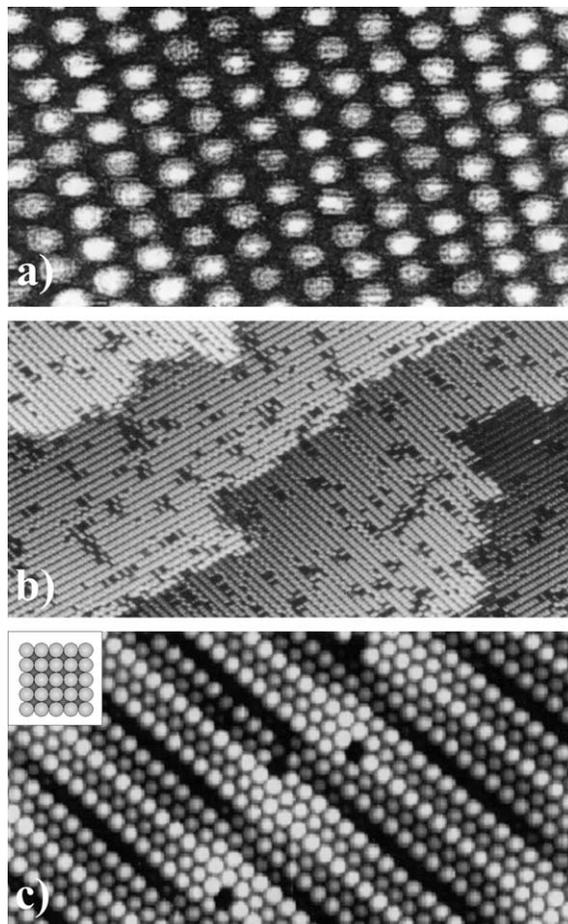

Fig. 1. Structure of surfaces as seen by STM: (a) clean Al surface (adapted from Ref. [1], with permission); (b) Large scale topograph of a Si(1 0 0) surface (from Ref. [2]. Copyright—1993 by Oxford University Press, Inc. used by permission of Oxford Univ. Press); (c) Image of the reconstructed Pt(1 0 0) surface (adapted from Ref. [3], with permission). The inset shows the arrangement of atoms in a non-reconstructed (1 0 0) surface.

posit on it. This is actually not so. Fig. 1b shows for instance the (1 0 0) surface of Si as determined by STM measurements [2]. Large irregular terraces with the nominal orientation are present but also a number of random steps and kinks are clearly visible. Fig. 1c gives another illustrative example. It shows a Pt(1 0 0) surface again as imaged by STM [3]. The inset in Fig. 1c shows the ideal positions that surface atoms of a (1 0 0) surface should have when the platinum single crystal has been cut (a square array). Obviously, the surface

atoms do not occupy such ideal positions but rather form a very elaborate pattern. The surface in this case is "reconstructed". A number of small pits are visible both in Fig. 1b and c, which are signaling the vacancy of several atoms in the topmost layer.

Even at the outset therefore, we are confronted with the difficulty that also "model" surfaces, prepared with the purpose of reducing the level of complexity, do present a relatively large number of defects and/or other anomalies.

When a surface interacts with an external flux of atoms and/or molecules, many phenomena may take place; some of the most important ones are sketched in Fig. 2.

Process no. 1 shows a diatomic molecule which impinges on a surface. On hitting the surface it has a finite probability p of sticking to the surface and a probability $1 - p$ of bouncing back in the gas phase. These molecules often form a chemical bond with the surface and choose a site which maximizes the binding energy. However, they do not reside long in the site where they have landed: if the surface temperature is high enough, they start migrating, jumping from one site to the next in a random way (see Process no. 2 in Fig. 2) giving rise to a 2D diffusion process.

The chemical bond that the molecule has formed with the surface weakens considerably the intramolecular bond so that the molecule may end up dissociating into its constituents; these, in turn, stick to the surface with strong chemical bonds (Process no. 3). Also, atoms originating from the dissociation process are mobile on the surface and during their 2D random walk, they may encounter another chemisorbed particle (atom or molecule) with which they might combine forming a new molecule, which may in turn leave the surface (Process no. 4).

A surface however is not a simple inert checkerboard. Upon adsorption of a foreign atom or molecule, it undergoes a local deformation; the atoms of the surface, while forming new chemical bonds with host particles, modify the structure of the bonds with the underlying bulk. When potassium is adsorbed on an Al(1 1 1) surface, for instance, it induces a rumpling of the first layer such that the Al atoms directly beneath the K atoms
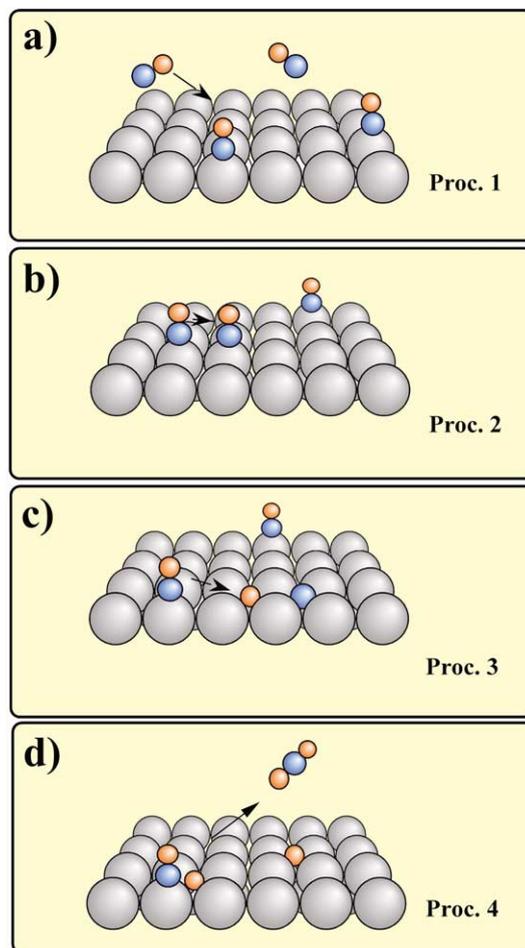

Fig. 2. Sketch of a number of elementary surface processes taking place on a surface exposed to an external atmosphere of reacting gases. Panel (a) shows the process of the adsorption of a diatomic molecule; Process no. 2 in panel (b) shows an elementary step of diffusion, while in panel (c) a process of dissociation is sketched. Finally panel (d) shows the reaction step of combination between two ad-particles, producing a molecule which is released in the gas phase.

are displaced towards the bulk by as much as 0.25 Å [4].

For stronger interactions the adsorbate may cause reconstruction of the underlying surface, which can range from a simple distortion of the elementary cell, up to a complete rearrangement of the surface atomic geometry.

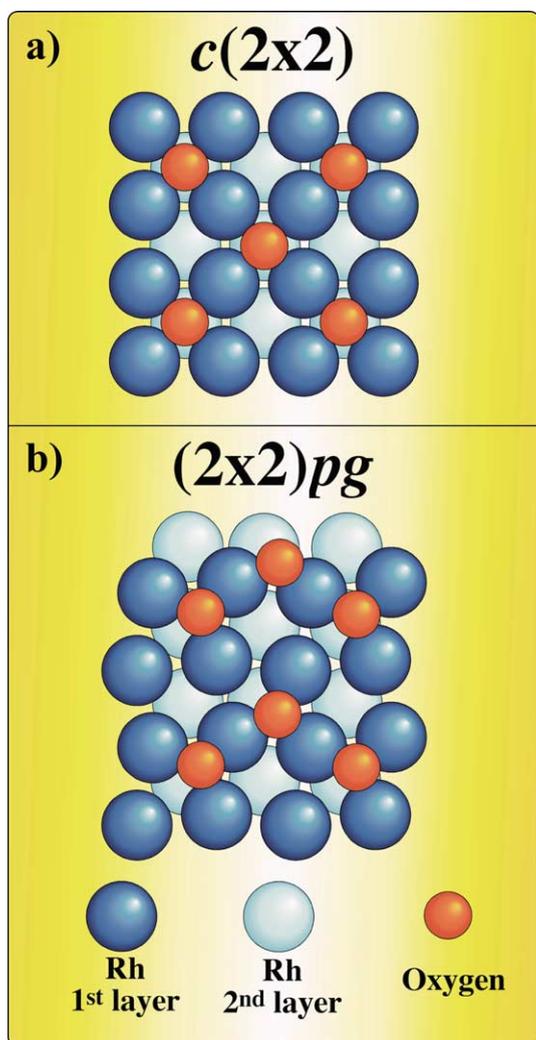An example of the first type of reconstruction is shown in Fig. 3. While Fig. 3a shows a c(2 × 2)

Fig. 3. Adsorbate overlayers on a (1 0 0) f.c.c. metal surface at 0.5 ML coverage: (a) regular c(2 × 2) structure; (b) (2 × 2) pg structure formed by oxygen on Rh(1 0 0).
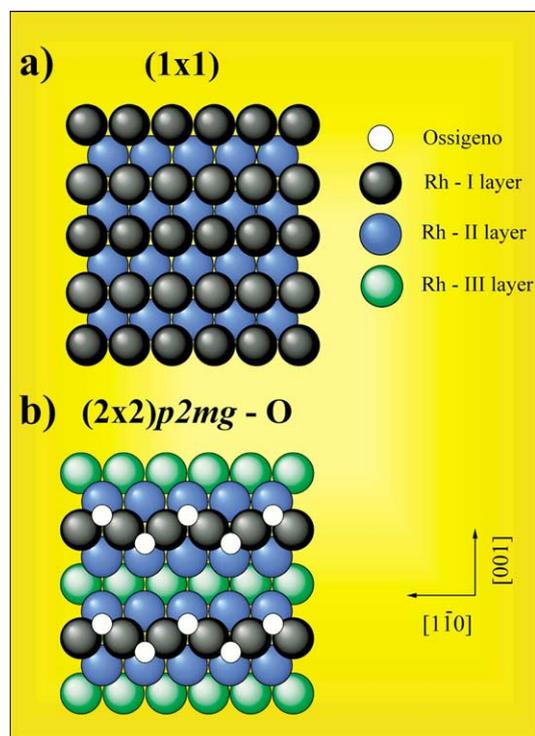

Fig. 4. (a) Structure of a clean Rh(1 1 0) surface; (b) change of structure upon adsorption of 0.5 ML of oxygen. The morphology of the reconstructed (2 × 2) p2mg surface implies a major process of mass transport during formation.

structure, which is the most common formed by an adsorbate on a (1 0 0) surface of a face centered cubic crystal at a coverage of 0.5 ML, the distortion induced by oxygen adsorption on Rh(1 0 0) is clearly visible in Fig. 3b. When the coverage approaches 0.5 ML (mono-layers, ML), the elementary cell elongates from the original square to a rhombus and the oxygen sits in one of the corners forcing a new surface symmetry [5,6].

Fig. 4a shows the structure of a Rh(1 1 0) surface while Fig. 4b shows the same surface after 0.5

ML adsorption of oxygen [7]. A considerable mass transport of rhodium atoms takes place in this case and gives rise to a (2 × 2) "missing row" reconstruction, characterized by depressions three atomic steps deep.

Surface reconstruction, whether spontaneous or induced by an adsorbate, is an important phenomenon since it implies, besides a change in the geometry, a strong change of the electronic structure and of the chemical reactivity of the surface.

In order to obtain an understanding of complex surface processes like catalytic reactions or the formation of metal–semiconductor interfaces, we need to know which are the various species that participate in the process, how they are bound to the surface and what are the activation energies of the single elementary steps they go through.

The detection, identification and characterization of these elementary processes, however, is a

very challenging task: we are dealing with a physical system which consists merely of a 2D phase and, therefore, extremely surface-sensitive experimental tools are needed.

Ideally, in order to fully describe the behavior of atoms and molecules on a surface, we would require insight at atomic length scale and at the characteristic times of elementary step evolution (i.e. sub-picosecond time resolution).

3. Selected experimental results

In order to address these challenging tasks, in the last 30 years or so, surface scientists have developed an arsenal of different experimental techniques [8]. In the following, we describe some of the exciting results which have been obtained in recent years with two of these techniques, STM [9] and atomic force microscopy(e) (AFM) [10].

Structural information at the required spatial resolution has been obtained by these scanning probe techniques, which, however, still have poor time resolution and a limited "chemical" sensitivity, although a number of groups have demonstrated the possibility of acquiring STM images displaying "chemical contrast", mostly in the case of metallic alloys [11–14].

The STM is generally capable of acquiring atom-resolved images of the uppermost surface layer of a conducting solid. Beautiful and dramatic images of the atomic arrangements have been obtained for a rather large number of metal and semiconductor surfaces. Most spectacular in the history of surface science has been the visualization of the geometric structure of the (7×7) reconstruction of the Si(1 1 1) surface [15]. This complex reconstruction had proven to be one of the most intriguing problems in surface science. Due to the fact that this particular reconstruction extends to a few layers underneath the surface, the complete determination of this structure had to wait until the detailed transmission electron diffraction measurements of Takayanagi et al. [16].

Recently, some very impressive STM experiments have been performed in Ertl's group in Berlin, Germany, and in Besenbacher's group in

Århus, Denmark, for characterizing the diffusion processes of adparticles on surfaces (Process no. 2 in Fig. 2b).

Previous macroscopic experiments for determining adsorbate diffusion constants have encountered severe difficulties. Even a well prepared single crystal surface in fact, exhibits defects (mostly atomic steps, kinks and impurities). Hopping energies at sites with different local structure may widely differ and macroscopic experiments can only probe "effective" diffusion parameters averaged on many different elementary hopping processes.

By using newly developed fast STMs, capable of acquiring up to 20 images per second (typically 100 Å $\times$ 100 Å wide) while still conserving atomic resolution, these groups have been able to follow the dynamic behavior of individual host atoms on several metal surfaces. The method they have implemented consists in taking a long sequence of pictures of the same region of the surface and record those atoms which have moved by one lattice parameter from one frame to the following one.

Counting the atoms that have not moved yields the probability P that atoms are still found on their original site at time t. If we can assume that the jumps are statistically independent, then $P(t) = \exp(-t/\tau)$, where τ is the mean time an adatom spends on its adsorption site. The jumping rate v is just the inverse of τ.

Fig. 5 shows for example, an image obtained from an STM movie of nitrogen atoms adsorbed on a Fe(1 0 0) surface [17]. In the inset of the figure, open circles mark the original positions of four N atoms and it can be seen that in the time lapse between two pictures, three atoms have moved by one lattice parameter.

By performing the experiment at several different temperatures, it is found, as expected, that the elementary jump rate follows the law of an activated process, i.e.:

$$v = v_0 \exp(-E_d/k_B T)$$

where E_d is the energy barrier the atoms have to surmount, v_0 is a pre-exponential factor generally referred to as "attempt frequency" and k_B is the Boltzmann constant.
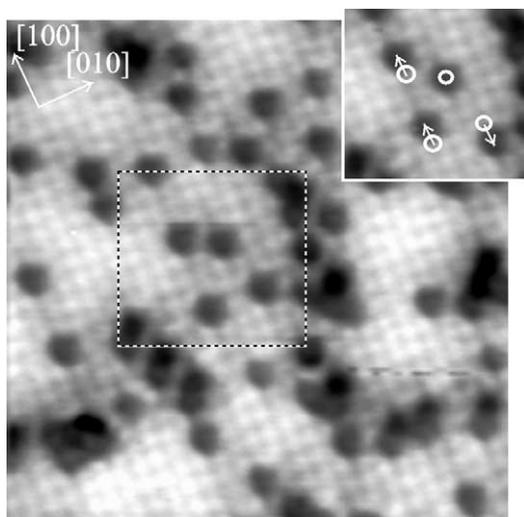
Fig. 5. STM image obtained from an STM movie of nitrogen atoms adsorbed on a Fe(1 0 0) surface at 300 K. N atoms are imaged as dark spots. The inset shows an area (marked by a dashed rectangle) 62 s later. Open circles in the inset mark the original position of four isolated N adatoms (from Ref. [17], with permission).

Fig. 6. STM image of a Ru(0 0 0 1) surface after the dissociative adsorption of 0.3 L of NO at 315 K, showing two terraces separated by a monatomic step (black almost vertical stripe). The black dots are N atoms. Their concentration profile signals that NO molecules have dissociated at the step (reprinted with permission from Ref. [22]. Copyright—1996 American Association for the Advancement of Science).

The values of the pre-exponential v_0 and of the energy barrier have now been determined for several systems [17–20].

These accomplishments must be considered as a real breakthrough: having isolated a single elementary step of a surface process, this becomes now amenable of a meaningful comparison between theory and experiment, which is the only foundation for advancing our understanding. A comprehensive review of diffusion phenomena of adsorbates on metal surfaces has recently appeared in the literature [21].

Concerning the use of STM in understanding the elementary steps of a catalytic reaction, the last four years or so have witnessed some really spectacular results. Zambelli et al. [22] for instance, addressed Process no. 3 in Fig. 2c in the case of dissociative chemisorption of NO (a decisive step in the catalytic reduction of nitric oxides), on the (0 0 0 1) surface of ruthenium, which is known to be the most selective catalyst for this reaction.

They exposed the surface at room temperature to a small dose of NO (0.3 L) and recorded an STM topography 0.5 h after exposure. The results
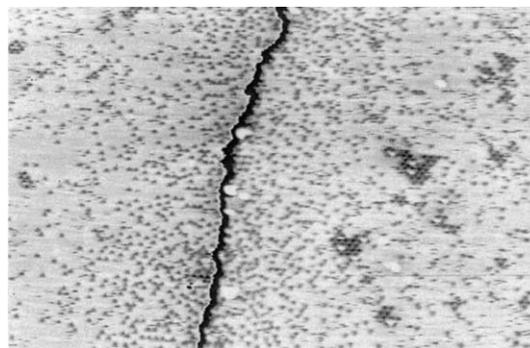
are shown in Fig. 6. The ragged line which crosses the figure almost vertically is a monoatomic step (these defects are always present even on the best prepared surfaces). A large number of small dark dots is visible on both sides of the step and are identified as N atoms originating from dissociated NO molecules. The small clusters at larger distances from the step are islands of oxygen atoms. These identifications were made on the basis of previous experiments with pure N or O layers in which it had been found that O atoms tend to cluster in islands with a (2×2) structure, while N atoms remain randomly distributed [23]. The NO molecules at 300 K and at low coverages are extremely mobile and are not detectable by STM. The picture which emerges from the distribution of the product atoms is very intriguing. The NO molecules, once adsorbed, diffuse rapidly across the terraces of the surface until they meet a step. Here, they apparently have a very high probability of dissociating. After dissociation, O atoms move relatively rapidly away from the steps. Nitrogen atoms move more slowly so that the image shows a diffusion profile of N atoms with its origin at the step. This interpretation has been later confirmed by detailed density functional theory calculations [24].

Both theory and experiment demonstrate clearly that the Ru(0 0 0 1) surface is not uniformly

active for the process of dissociation of NO, but, rather, that the steps are highly preferential sites. This notion of special "active sites" on surfaces is an old one in catalysis; however, their exact nature and the mechanism by which they act, have remained elusive for a long time.

It is interesting to note that both sides of the step are covered with a comparable number of N atoms. Observing that a N atom does not cross the step upon dissociation, this means that NO molecules approaching the step, both from the lower and from the upper adjoining terrace, dissociate with about the same probability. From this observation Zambelli et al. conclude that the reaction takes place at the frontmost metal atoms at the step.

Besides confirming directly the concept of "active site" in catalysis, this experiment demonstrates that the kinetics is influenced by surface structure at sub-nanometer level and confirms that "macroscopic" experiments can only measure an overall reactivity which results from weighted contributions from various surface structure elements at the microscopic level.

The elementary step by which a molecule and an atom adsorbed on a surface react and their end products is released in the gas phase (Process no. 4 in Fig. 2d) is well exemplified by the oxidation of CO, for instance on Pt(1 1 1).

This is one of the most studied model-like catalytic reaction also because it represents a key step for the removal of CO from exhaust gases.

Despite the detailed knowledge of many aspects of the CO and O reaction, the usual macroscopic experiments have not been able to determine a mechanistic model completely consistent with all the features of the measured kinetics.

In a very elegant experiment, Wintterlin et al. [25] have recently observed this reaction with STM and were able to atomically resolve the reactants, monitor their reactions as a function of time and derive a quantitative rate equation, based solely on the statistics of the atomic process.

The experiment was performed as a titration, by first covering the sample with a submonolayer of oxygen and by exposing it afterwards to a constant CO pressure.
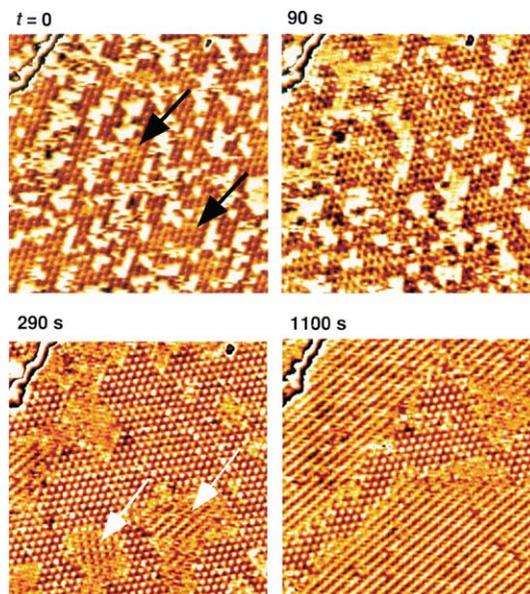

Fig. 7. Series of STM images, recorded during reaction of adsorbed oxygen atoms with co-adsorbed CO molecules at 247 K, from the same area of a Pt(1 1 1) crystal (reprinted with permission from Ref. [25]. Copyright—1997 American Association for the Advancement of Science). Black arrows in the $t = 0$ image mark two of the (2×2) oxygen islands. The white arrows, after 290 s, shows the formation of some c(4×2) CO islands.

As shown in Fig. 7, after preparation (time $t = 0$), the oxygen atoms (imaged as dark dots) form small irregular islands with the known (2×2) structure (two of them are indicated by black arrows). The white patches represent bare platinum areas. Adsorption of CO on this surface produces (after 90 s) a compression of the oxygen layer (the dark dot covered areas are now larger). The total area covered by oxygen has not changed at this time and the CO molecules, that are certainly present on the clean Pt areas between oxygen islands, are not visible because of their high mobility.

After 290 s of CO exposure, the oxygen islands start to shrink, signaling the beginning of the reaction. The areas not covered by oxygen show now (see white arrows) a c(4×2) structure, distinctive of near saturation CO adsorption. By this time in fact, the CO molecules are closely packed and therefore practically immobilized, becoming

resolvable by the STM. The image taken after 1100 s shows that the c(4 × 2) areas continue to grow at the expense of the (2 × 2) oxygen areas, demonstrating the progress of the reaction. After 2200 s the oxygen has disappeared, the surface (not shown) is completely covered by CO and the reaction is completed.

This experiment is illuminating in many ways:

(i) it clarifies one of the possible origins of the so called "induction time" (which is the delay sometimes observed from the moment both reactants are present on the surface, to the time when reaction starts to occur). In the conditions of the experiment, it originates from the time needed by the process of CO adsorption from the gas phase to fill up the areas not covered by oxygen. This suggests that at low coverages, the repulsion between CO_{ads} and O_{ads} is strong enough to prevent reaction. Only when the surface is filled up with reactants and the CO islands push against the border of O islands, the reaction begins;

(ii) in the conditions of the experiment the reactants were clearly not distributed randomly but were forming separate domains and the reaction was only taking place at the boundaries between the (2 × 2) oxygen islands and the c(4 × 2) CO domains.

The STM images were also amenable of quantitative treatment and the authors evaluated the CO_2 production rate by determining the (2 × 2) oxygen fraction as a function of time. Repeating the process at different temperatures, it was then possible to evaluate the kinetic parameters of the reaction.

This work is a beautiful and so far unique example of how, by observing elementary steps of catalytic phenomena at the atomic scale, one can derive in a unique way the kinetics of the process directly from the microscopic mechanism.

4. Semiconductor elementary surface processes and new device fabrication

We have presented so far examples of elementary surface processes which are mainly relevant to the modeling of simple catalytic reactions. Some of the best catalysts are transition metals like platinum or rhodium and the examples have been chosen accordingly.

In this class of phenomena, the surface which catalyzes the transformation of reactants into the reacted species returns to its original conditions after the reaction has taken place. When completed, the reaction, at least in principle, leaves the surface essentially untouched and unmodified.

On semiconductors, on the other hand, the elementary phenomena which are of highest interest are those aimed at modifying the surface, with the purpose of device fabrication. In the following, we present some of the most relevant processes which take place during deposition reactions in which one or more layers of a host semiconductor species are deposited on a semiconductor surface.

Remarkably, in the last two decades or so, the quest for fabricating new materials with desired electronic and microscopic properties down to the atomic scale has had a tremendous impact on research on semiconductor surfaces and on the development of new micro and optoelectronic devices. One very important method which has been developed for this purpose is epitaxial growth.

In principle, three epitaxial growth modes have been studied and classified:

1. layer by layer growth in lattice matched systems (Frank–Van der Merwe);
2. the island growth mode (Volmer–Weber);
3. the layer by layer, then island growth mode (Stranski–Krastanov, SK) in lattice mismatched systems.

One typical example of semiconductor on semiconductor growth which we would like to discuss here is layer by layer growth followed by island formation, which takes place in the SK growth mode in heteroepitaxy [26–28]. The strain caused by the difference in lattice parameters between the materials employed, naturally leads to island formation after the completion of a thin (a few monolayers thick) layer, the so called 2D "wetting layer", on top of a template substrate. At the early stage of island formation, the islands can be free of defects (coherent), whereas during further growth defects and dislocations are introduced.

Strain relaxation and island formation in lattice mismatched semiconductor systems in the SK growth mode have been studied in great detail in the (InGa)As/GaAs and Si/SiGe material systems. Strain relaxation in this stage is believed to occur due to the elastic deformation of the substrate and at the free edges of the islands, and possibly to intermixing between the atoms of the constituent species; the elastic energy reduction outweighs the cost of additional surface energy due to island formation to form a lower energy configuration than that of the planar strained film. It has also been shown that coherent islands are energetically favored over dislocated islands below a critical size with a distinct coherent-to-incoherent transition for continued growth or ripening.

In the last decade or so quantum dots (QDs) have become particularly interesting, both from a fundamental and a technological point of view. The goal is therefore to fabricate these QDs, i.e. 3D structures which are so small that the charge carriers inside them find themselves confined in atomic-like energy levels. The possibilities of future applications are quite obvious: controlling the size and spatial distribution of the islands would enable to tailor the energy levels to one's needs, leading for example to the fabrication of completely new optoelectronic devices.

In the area of compound semiconductors such as InGaAs/GaAs and InAs/GaAs, self-organized QDs have been intensively studied and successively employed to build lasers with a low threshold current. In this context, size uniformity of the dots is the crucial aspect.

In the course of further control of the formation of (InGa)As islands in the SK growth mode it is desirable to achieve vertical ordering as well as lateral ordering towards the formation of 3D arrays of 'dots'. Vertical alignment of dots in the growth direction during the subsequent deposition of multiple layers of islands separated by thin spacer layers has been observed by several groups in the (InGa)As/GaAs and Si/SiGe systems and is attributed to the presence of non-uniform strain fields during the growth of successive layers.

This vertical alignment of the islands during the growth of successive layers has been reported several times [29], and it is probably due to the formation of a region of tensile stress above an island, which favors the positioning of islands on top of it, leading to column stacking of islands.

On the other hand, heteroepitaxial Ge/Si alloys seem to be promising materials for both microelectronic [30] and optoelectronic [31] applications: due to the fact that Si still rules the semiconductor market, the possibility of integrating micro and optoelectronics on the same Si chip is one of the main objectives in this field of research.

The main questions to be pursued in this context are: how the strain leads to island formation, and the role of Ge–Si intermixing; both questions have been addressed in a series of recent papers [30–35]. Besides, it is not yet possible to grow islands of desired size, shape and density, partly because the experimental results available today are lacking detailed knowledge of the SK growth dynamics, particularly on the atomic scale.

Again, in order to gain complete insight on the details of these growth processes, fast atomic-length-scale monitoring is necessary.

5. Change of the reconstruction in the Ge/Si system

As was discussed earlier, it is well known that in many lattice mismatched heteroepitaxial systems the SK growth mode is observed; this consists initially of the formation of a 2D strained layer. During the growth of thicker layers, the increasing misfit strain leads to a transition to different growth morphologies: the formation of coherent, dislocation-free 3D islands or the formation of misfit dislocations are efficient ways of relieving the misfit strain, at least partially. Besides this transition to different growth morphologies during the later stages of growth, even during the formation of the initial 2D layer, the surface reconstruction may change in order to accommodate for the increasing strain energy.

For example, in the case of Ge epitaxy on Si(0 0 1), a $(2 \times N)$ reconstruction is observed on the 2D strained layer (the wetting layer); this reconstruction consists of a periodic array of missing dimers of the (2×1) dimer reconstruction: every Nth dimer of the (2×1) reconstruction is missing.

Additionally, the reconstruction periodicity (N) is dependent on the stoichiometry of the wetting layer, i.e. the amount of Si/Ge intermixing [36]. (The wetting layer, which has been introduced previously, is a layer a few MLs thick: after the completion of it, layer by layer growth is not favorable any more, and therefore after the critical thickness is reached the growth proceeds by island nucleation.)

In the case of Ge deposited on Si(1 1 1) on the other hand, the reconstruction gradually changes from the typical 7×7 reconstruction of the Si(1 1 1) surface to the 5×5 of the Ge–Si wetting layer. This is an interesting phenomenon: it means that the reconstruction is still hexagonal, but with a different degree of symmetry.

After deposition of 0.45 ML of Ge the 7×7 reconstruction is maintained; this has been observed by STM and was also confirmed by the RHEED pattern, that can probe a larger and deeper region of the surface. The absence of islands on the terraces and of reconstructed ($2 \times N$) areas of Ge suggests the diffusion of Ge atoms into the Si substrate. As proposed in the case of sub-monolayer deposition of Ge on Si(0 0 1) surfaces, Ge might exchange places with Si and the mobile Si might diffuse to the substrate step edges (displacive adsorption).

When the Ge coverage exceeds 3 ML [32,33], several 3D islands appear at random locations on the surface. At the beginning they have a triangular shape (truncated triangular pyramids, or tetrahedra), average lateral dimensions 500–1000 Å and are about 1 ML high. It has been suggested that this morphological transition occurs when the free energy of the islands is lower than that of the strained layer. At 9 ML coverage two kinds of islands are visible: small, tall islands (typically 1800 Å wide × 100 Å high); large and ripened flat islands (average dimensions 3500 Å wide × 25 Å high). It is argued that, after nucleation, the islands grow vertically up to a critical value at which the strain energy introduces a morphological transition with the possible formation of dislocations. Subsequently the islands grow laterally, apparently drawing material from the top or collapsing together with other islands. This process is called ripening and leads to the formation of flat,
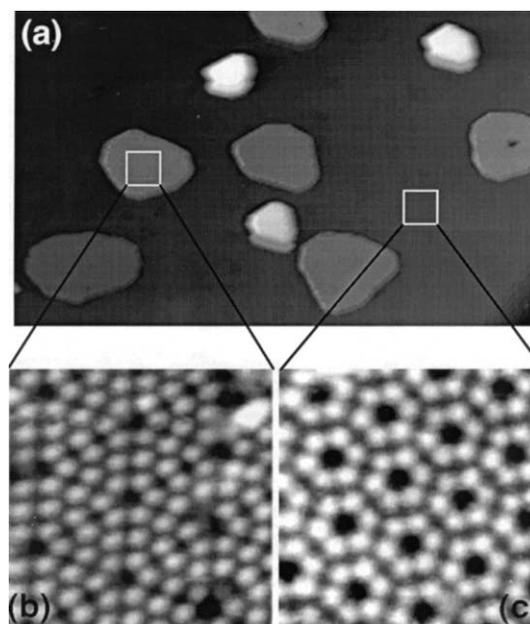

Fig. 8. STM images of a Ge–Si(1 1 1) surface after deposition of 9 ML of Ge. Two different kinds of islands are visible in (a): tall and triangular shaped (white) and low and rounded (gray). Magnifications 80×80 Å^2 (b) on the island's top and (c) on the substrate display the 7×7 structure of the former and the 5×5 of the latter (from Ref. [32]).

round islands. Some of these islands display a hole at their center, whereas other ones display a depletion surrounding them. These features should be related to strain and intermixing [37–40]. Enlarged STM shots on the top of the islands (both for strained and ripened islands) and on the substrate display the 7×7 structure of the former and the 5×5 reconstruction of the latter (see Fig. 8).

6. Results for intermixing, local spectroscopy

Recently, Boscherini et al. [34,35] have provided direct evidence of Si–Ge intermixing in self-organized strained and unstrained Ge QDs grown on Si(1 0 0) and Si(1 1 1) surfaces, also determining a quantitative measurement of the average composition. This was done by exploiting Ge K-edge X-ray absorption spectroscopy (XAFS); the measurements were taken at the ESRF in Grenoble

(France). The XAFS technique is a powerful tool for the study of the local chemical composition of solids and surfaces, its usefulness resting on the fact that it is a local spectroscopy, and therefore it does not require a sample exhibiting long range order.

Previously [32,33,41] several STM studies had argued the occurrence of some degree of intermixing in this heteroepitaxial system, but no conclusive answer had been found.

The results reported in Refs. [34,35] have provided a direct answer to the question of intermixing in these systems; the authors discuss their observations in terms of the energetics of island formation. It is argued that the important energy terms are in fact the strain energy, the surface energy of epilayer and substrate and, in the case of relaxed or partially relaxed layers, the dislocation formation energy. Intermixing can have an important role in decreasing the strain energy; in fact, the total strain energy of an ensemble of dots is given by a volume integral in which the elements of the strain tensor appear quadratically. The magnitude of the strain tensor elements depends linearly on the difference between the local free lattice parameter (in each direction) and that imposed by the SK growth on the substrate. Since the free lattice parameter can be reduced by intermixing it follows that diffusion of Si into the Ge dots will reduce the strain energy per atom.

In principle it could seem strange that such a high level of intermixing should occur at the Ge–Si interface, at the relatively low temperatures that have been used for growth: the bulk interdiffusion coefficient of Ge in Si has been estimated [42] to have an activation energy of 3.93 eV, which would lead to an extremely slow interdiffusion rate.

In a series of recent papers [43,44], Bottomley has proposed new theoretical insight on the formation of semiconductor QDs, with particular interest in the phenomenon of intermixing.

His main, quite radical, idea is the following: he proposes that the large heteroepitaxial stress present on semiconductor surfaces during heteroepitaxy (in particular for InAs on GaAs(0 0 1), but also the case of Ge on Si(0 0 1) is briefly discussed in his papers) causes InAs to melt when deposited on GaAs(0 0 1) at about 770 K. This naturally leads to mixing with the substrate in order to obtain a local minimum of the Gibbs free energy of the liquid phase. The liquid phase clearly facilitates mass transport, leading to QD formation. This is a phenomenon which is strictly related to surface properties, and it has no bulk analogue.

His calculations predict that island formation occurs after about 2 ML of liquid InAs material accumulate in order to minimize the surface tension, but without effectively reducing the net coordination of the liquid phase atoms.

When applied to the Ge/Si(0 0 1) system for typical growth temperatures such as about 970 K (about 700 °C), the calculations again predict a liquid phase, and he expects that in the limit of equilibrium thermodynamics the molten Ge should mix with the Si substrate to yield an alloy of approximate composition $Si_{0.5}Ge_{0.5}$.

In principle, if one writes down the expression of the thermodynamic force acting on a Si and on a Ge atom at opposite sides of the Ge/Si interface, one would find that they have opposite signs, meaning that Si wants to diffuse into the Ge layers, and vice versa.

Clearly hydrostatic pressure has the effect of reducing the melting point of both Ge and Si; recent works [45,46] measure an incremental film stress of up to 5 GPa for Ge grown on Si(0 0 1) and up to 7 GPa for Ge on Si(1 1 1), while theoretical calculations [47] also predict an isotropic stress in the range 6–9 GPa for Ge on Si(1 1 1) and about 3 GPa for Ge grown on Si(0 0 1) (the stress is larger under the islands, smaller in island-free regions). Therefore the intuition that the compressed Ge should become more mobile (even without actually melting) is qualitatively justified. This means that the process of atomic exchange (which is always present, but too slow at the relatively low temperatures used for growth) can be strongly accelerated in the Ge layers which are compressed, but not into the Si layers which are expanded.

We observe here that we are not in the presence of hydrostatic pressure, but of planar stress. One can however expect that uniaxial stress should always favor fusion, whatever its sign, either compressive or tensile; in fact both cases imply an increase in elastic energy, which is obviously absent in the liquid phase.

7. Self-organization of nanostructures versus lithographic techniques

Performance and integration density of large-scale-integrated circuits are growing fast as time passes, despite the limitations that were predicted just a few decades ago. At the same time, new techniques for nanofabrication which do not make use of conventional lithography are attracting interest and attention worldwide, for the purpose of processing the new generation of micro and optoelectronic devices. This is due to the fact that optical lithography is presently not capable of fabricating structures with lateral resolution smaller than a few hundreds of nanometers, whereas new device effects using single electron and other quantum effects require structure control of just a few Å.

One recent potential breakthrough in nanofabrication is represented by the development of techniques which employ scanning probe microscopies [48]. Indeed, as was shown several years ago by Eigler and co-workers [48], the STM is a surface-science tool which is both capable of fabricating and studying nanostructures on the atomic scale; one example is the manipulation of single atoms on a surface using the STM. The main problem with these techniques is the fact that, due to their serial nature, they cannot be applied directly to the large-scale production of integrated devices.

In order to achieve wafer-scale control, many authors [49] have been trying to develop self-organization techniques; the idea here is simply to "let nature do it herself": nanostructures are formed by spontaneous growth, without the use of lithographic techniques.

It is generally believed that self-assembling processes have the disadvantage of poor controllability of size uniformity and arrangement of positions; however, the improvement of control would obviously lead to a breakthrough, because in this way nanostructures could be simultaneously developed on the whole wafer surface.

A recent review article by Ogino et al. [50] has shown that self-organization can potentially be exploited to produce uniform and artificially designed nanostructure patterns, provided that crit-

ical surface features such as reconstruction, atomic steps and the phase boundaries of reconstructed domains can be controlled.

Once surface control is achieved, these critical features may be used as templates for controlled growth of hetero-nanostructures. This is especially
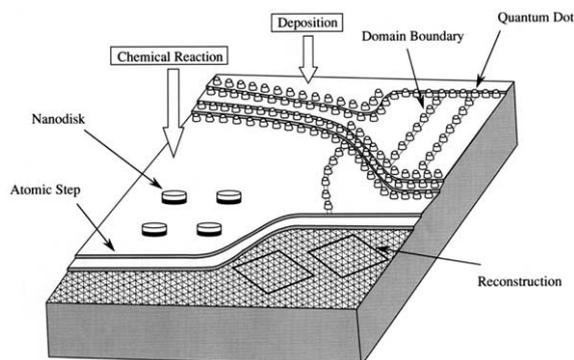

Fig. 9. The idea of nanofabrication based on surface structure control. Nanowires and QDs are self-organized on Si surfaces by controlling reconstruction, atomic steps, and reconstructed domain boundaries, which are to be used as nanofabrication templates (from Ref. [50], with permission).
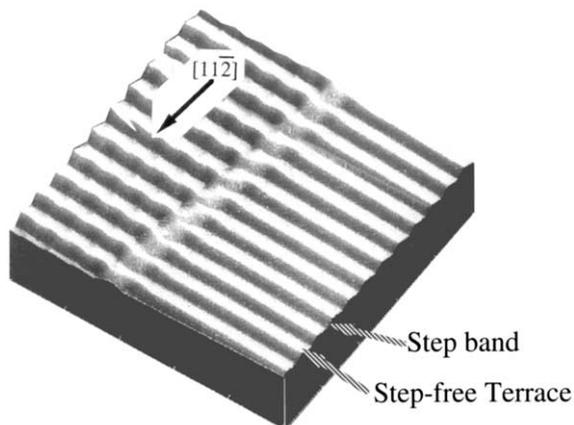

Fig. 10. AFM image of the step bunches that are formed on a Si(1 1 1) surface. The density of steps on the reconstructed surface depends critically on the flashing conditions. The Si substrate is misoriented toward the $\langle 11\bar{2} \rangle$ direction by 1.5° from the exact (1 1 1) surface. The patterns used to control the step arrangement were hole arrays with a pith of 3.5 μm (right region) and 4.0 μm (left region) (from Ref. [50], with permission).
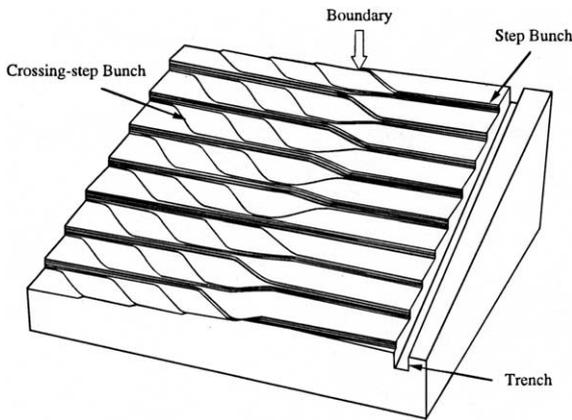
Fig. 11. Schematic of the step network formed as shown in Fig. 10. The step network in the left region consists of main step bunches steps crossing the terraces, whereas that in the right region exhibits only main bunches. This difference is due to the boundary conditions (from Ref. [50], with permission).

true in the case of Si surfaces, since their structure can be controlled down to the atomic level [50] (see Figs. 9–11).

Fig. 9 shows the key idea of nanofabrication: the approach is based on surface structure control. Nanowires and QDs are self-organized on Si surfaces by controlling reconstruction, atomic steps, and reconstructed domain boundaries as selective templates for nanofabrication.

Fig. 10 displays a Si(1 1 1) surface with a regular step arrangement and regular spacing of terraces between two consecutive steps; the substrate is misoriented toward the $\langle 1 1 \bar{2} \rangle$ direction by 1.5° with respect to the exact (1 1 1) surface. Fig. 11 shows a schematic of the step bunching network and cross step bunching on a Si(1 1 1) surface, referred to the surface shown in Fig. 10.

The idea here is to control the formation of steps and the width of the terraces, for the purpose of using the terraces as templates for the growth of nanostructures. If one wants to envision the production of optoelectronic devices using new materials based on Si substrates, it is essential to achieve an alignment of the islands on the surface. This can be obtained in principle by controlling the stress on the surface, for example by patterned implantation of gas (such as Ar) layers buried deep within the samples [51] leading to re-

gions of enhanced/reduced stress on the topmost layers of the surface. It has in fact already been shown that the control of surface stress leads to a higher concentration of adatoms on tensile stress regions [51].

The process is divided in "elementary" steps, as follows:

1. The first step is surface structure control, down to the atomic level; this is possible in principle for Si(1 1 1) surfaces; so far the Si(0 0 1) surface is the most widely used but there are many good reasons for trying to employ the Si(1 1 1) surface. For example, recent studies have shown how it is possible to create large terraces on this surface [52,53].
2. The second stage is the fabrication of semiconductor hetero-nanostructures whose formation sites are determined in advance, by controlling surface structure.
3. Finally, electronic devices require insulating layers and conducting layers in addition to the semiconductor nanostructures: the third stage is the fabrication of alternate semiconductor/insulator/conductor nanostructures.

The basic idea of this approach is the compatibility of atomically controlled nanofabrication and wafer scale integration. In current Si-MOS (MOS: metal oxide semiconductor) technology, the Si(0 0 1) surface is exclusively used, mainly for two reasons: because it is more easily oxidized, therefore allowing easy lithographic patterning, and because its Si/SiO$_2$ interface exhibits a lower density of defects compared to other surfaces.

However, in trying to control self-organizing nanostructures, the Si(1 1 1) surface has the advantage that an atomically flat surface and a well-defined step-terrace structure can be easily obtained, by a combination of thermal and chemical treatment.

8. Nanofabrication and atomic-scale manipulation using scanning probe microscopies

In a visionary speech entitled "There's plenty of room at the bottom", about four decades ago

Richard Feynman speculated on the fascinating properties of matter made by arranging "the atoms one by one the way we want them" [54].

Since the mid 1970s, before the invention of the STM, low dimensional confinement structures called quantum wells could be made by using growth techniques such as molecular beam epitaxy and metal-organic chemical vapor deposition. High-energy barriers at both sides of the quantum well confine the charge carriers into a 2D layer, giving experimental proof of the particle-in-a-box quantization "textbook problem", in the thin epitaxial direction. Though these techniques have atomic control in the epitaxial growth direction, they do not allow us to artificially structure materials in the remaining two lateral dimensions: only this achievement would create total quantum confinement.

A variety of techniques that achieve lower dimensional structures—quantum wires (1D) and QDs (0D)—have been attempted with varying degrees of success. Combining 2D epitaxial technology with nanometer-scale lithographic techniques, it has been possible to carve out thin lines and dots. The quantum confinement of the electrons in these structures is reflected in the energy states of the wire or dot, measured by optical or electronic techniques. A final demonstration of the quantum confinement would be the spatial mapping of the standing-wave patterns of electrons inside the structure; until recently, however, the electron wavefunctions of low-dimensional structures could only be derived by inference.

Indeed, the idea of manipulating matter on the atomic scale seemed to be just a fascinating dream—or even an unreachable goal—just a couple of decades ago. The underlying fascination may have been motivated simply by scientific and technological opportunities, or from curiosity about the consequences of being able to 'play' with atoms, placing them in particular locations on a surface, using them as 'building blocks' to construct just about anything on a chosen substrate.

In a series of outstanding papers published in the last decade (Refs. [55–57] just to mention a few) Eigler and co-workers have shown that the advances reached in STM have made this prospect a reality: single atoms and molecules may be manipulated in a variety of ways by using an STM, and therefore structures can be built to a particular design, atom by atom (though allowing for some limitations due to practical problems).

In the first article [55], they report the use of STM at very low temperatures (4 K) to position individual Xe atoms on a single-crystal Ni surface with atomic precision. This capacity enables them to fabricate rudimentary structures of their own design, atom by atom, namely to actually *write words* on surfaces using individual atoms for constructing the letters.

They have used the fact that an STM tip may exert a force on an atom or molecule adsorbed on a surface; by adjusting the position and the tunneling parameters (in this case the voltage) of the tip it is possible to tune the magnitude and the direction of the force, so that the STM tip can push or drag an atom or molecule across a surface, with the adsorbate still remaining bound to the surface.

The decision to study Xe on Ni(1 1 0) was not casual. Rather, it was dictated by the necessity that the corrugation in the surface potential be sufficiently large for the Xe atoms to be imaged without inadvertently moving them, yet sufficiently small that enough lateral force could be exerted to move the Xe atoms across the surface. The experiments were performed using an STM contained in a UHV system cooled to 4 K. The main reason for using low temperatures is to prevent the Xe atoms from thermally diffusing across the surface after they have been positioned in the desired location.

In order to move a single atom, they begin by using the microscope in a normal (non-perturbative) imaging mode, by which they locate the atom which is to be moved and decide where to move it; then scanning is stopped and the tip is placed directly above the atom which is to be moved. The successive step is to increase the interaction between tip and atom, by lowering the tip towards the atom. Finally, the tip is moved to the target destination on the surface, dragging the Xe atom along with it. At this point the tip is again withdrawn, by reducing the tunneling current to the value used for imaging. This effectively terminates the attraction between the Xe atom and the tip,
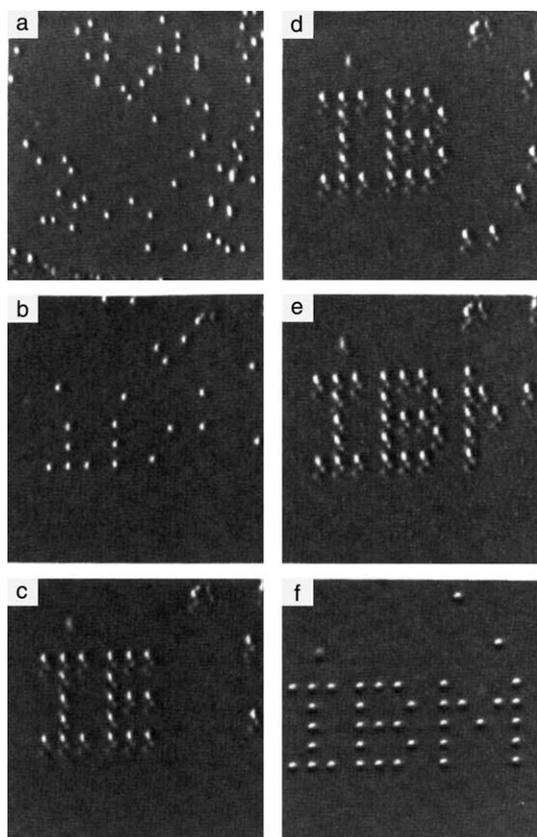
Fig. 12. A sequence of STM images taken during the construction of a patterned array of xenon atoms on a nickel (1 1 0) surface. The atomic structure of the nickel surface is not resolved. The ⟨1 1 0⟩ direction of the surface runs vertically. (a) The surface after xenon dosing, (b)–(f) various stages during the construction of the word IBM. Each letter is 50 Å from top to bottom (from Ref. [55], with permission).

leaving the Xe atoms bound to the surface at the desired location.

Fig. 12a shows the surface after Xe dosing. Each Xe atom appears as a 1.6 Å high bump on the surface, initially positioned at random locations. Fig. 12b–f shows various stages of the surface during the construction of the word "IBM". Each letter is 50 Å from top to bottom. At this gap impedance the interaction of the Xe atom with the tip is sufficiently weak to leave the Xe atom essentially unperturbed during the imaging process. The exact "periodicity" of the Xe atom spacing is derived from the crystalline structure of the underlying Ni(1 1 0) surface.

Creating or synthesizing 'custom' made structures is perhaps one of the most exciting applications of manipulation; it should be possible in this way to create totally new phases and structures of matter that are not normally accessible in nature: after creating these new structures, they can be investigated with the STM in the normal imaging and spectroscopy modes.

The main problem here, from a practical point of view, is the serial nature of the manipulations, versus parallel processes like lithography, which are therefore much faster and economically advantageous.

The STM has also been applied to induce chemical transformations on surfaces on the atomic scale by several groups of researchers [58]. Quite astonishing results have been recently obtained by Ho's group in Cornell. They were able for instance, to use the STM to break a C–H bond in a single acetylene molecule adsorbed on a Cu(0 0 1) surface [59]; they further proceeded to dehydrogenate the ethinil species to form dicarbon (CC) [59]. A comprehensive review of these fascinating results appears in this issue of Surface Science [60].

It has been shown that besides the breaking of selected molecular bonds, the STM can also induce a single bond formation. Lee et al. [61], have been able to form $Fe(CO)$ and $Fe(CO)_2$ molecules starting from Fe atoms and CO molecules adsorbed on an Ag(1 1 0) surface. More recently, Rieder's group [62] has demonstrated the feasibility of inducing all the steps of a surface chemical reaction by using an STM tip. They were able in fact to synthesize biphenil molecules starting from iodobenzene adsorbed on a Cu(1 1 1) surface. These groups have therefore demonstrated the concrete possibility of controlling chemistry at the spatial limit of individual atoms and molecules and have provided new insights into the nature of chemical bonds and reactivity.

The ability to manipulate matter with atomic scale precision suggests that single molecular synthesis is possible with the STM; there are several motivations for such synthesis. One could study how the environment of the reactants affects surface reactions, or how the conformation of reactants affects reaction barriers. If one could perform

such studies with an AFM it would be possible to study the forces between reactants as a function of conformation. Manipulation combined with force measurement seems particularly useful. For example, if one could measure the force on an atom during the sliding process, then it would be possible to map the potential between the atom and the surface. It should be possible to use the AFM to image and manipulate metal atoms on an insulating substrate, which would open the door to the study of electron transport in extremely small structures.

9. Perspectives for the future

One of the limiting factors towards our goal of a deeper understanding of surface phenomena is still the rather poor time resolution that most of the surface science techniques have. In practice, the time window in which we can observe phenomena is presently limited between a few milliseconds to a few thousand seconds. Extending this range to shorter times would be extremely beneficial to our investigation. On one hand, it would offer the possibility of detecting new intermediate species in kinetic processes which would be critical for a more in-depth understanding of the basic phenomena. As a second major benefit, higher time resolution would allow to explore processes at higher temperatures where, as a general rule, they tend to become much faster.

In recent years there have been several efforts to build ever faster STM and AFM instruments. While the time for the acquisition of a single frame (typically $50 \text{ Å} \times 50 \text{ Å}$) for a commercial instrument is of the order of several seconds, precision laboratory prototypes have been built which acquire up to 10–20 images per second, while still retaining atomic resolution [63–65].

In perspective, it is important to recall however that elementary dynamic phenomena at the atomic level take place on a surface at the femtosecond time scale, and even the recent impressive experimental advances (and foreseeable future ones) are missing this range by many orders of magnitude.

The second obstacle is the so called "pressure gap". While most of the surface science model studies carried out so far have been using very low pressures (less than about 10^{-6} mbar), real life processes are run at pressures many orders of magnitude higher.

Higher pressures mean very high coverage of the reactants. Many experiments have shown that, as the coverage of adsorbed species increases, the lateral interactions which develop strongly influence all surface processes. In this different regime all the elementary steps and the overall reaction rate may change dramatically.

It will be therefore compulsory to improve our present experimental techniques in order to be able to probe surface processes in higher environmental pressures. STM has already shown the capability of performing in situ high pressure studies of the atomic structure of surfaces. An outstanding example has been given very recently by Österlund et al. [66], who have been able to image a Cu(1 1 0) surface up to pressure of 1 bar of H_2, still maintaining atomic resolution.

10. Challenges and opportunities for a surface scientist

One of the problems which has hampered our progress so far, lies in the fact that experimental techniques, for the lack of space or time resolution (or both), usually observe an "ensemble" of different elementary steps and measure therefore parameters which are averaged out over several processes.

A great challenge for surface scientists is going to be the possibility of singling out and characterizing every step at the atomic level separately. This will require a substantial improvement of present techniques and probably, the development of new ones. The effort will be extremely exciting however, since it may also lead to the detection of new important "co-operative" many-body effects of which we had, so far, only occasional glimpses.

The goal of learning to design the atomic geometry of surfaces in order to confer them specific properties, is going to be another exciting challenge for the future. This endeavor would allow, for instance, to optimize the production rate and selectivity of catalysts or the physical properties

and size of semiconductor devices and would therefore be extremely rewarding from a practical point of view.

A rather impressive step towards the general goal of designing a catalyst from "first principles" has already been obtained by the combined effort of the theoretical group of Nørskov and the experimental group of Besenbacher. In a series of papers, they have presented a beautiful example in which the full step has been taken from atomistic surface science studies of a model system to the design of a new alloy catalyst for the steam-reforming catalytic reaction [67]. This is just an example which shows how a combined effort and a strong interplay between theory and experiment has produced significant advances in a very demanding field. The collaboration between theory and experiment is pursued by many surface science groups around the world, often producing very fruitful results. An even stronger interplay between theory and experiment would be very rewarding and should be further pursued and encouraged.

Finally, an extremely challenging task which is going to bring a lot of new opportunities for the future, is to enter the arena of bridging the gap between surface model systems and real surfaces, with the ultimate aim of achieving a fast technology transfer between research laboratories and high-tech industries.

Although surface science is a very demanding field of research, both in terms of experimental and theoretical resources, in its short history very remarkable results have been obtained in understanding surface phenomena at the atomic level, and new challenges are awaiting us in the near future in this exciting interdisciplinary field which has never been more lively.

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