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Alberto Pimpinelli and Jacques Villain
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Morphology of a crystal surface

Je ne me persuade pas aisément qu'Epicure, Platon et Pythagore nous aient donné pour argent comptant leurs Atomes, leurs Idées et leurs Nombres. Ils étaient trop sages pour établir leurs articles de foi de choses si incertaines et si débattables.

Montaigne (*Essais*, II, 12)

I can hardly convince myself that
Epicurus, Plato and Pythagoras
have sold us for sound
their Atoms, their Ideas and
their Numbers. They were
too wise to found their belief
on such uncertain and questionable things.

Twenty five centuries after Democritus, we are now able to see individual atoms, or at least small groups of them, through a variety of electron microscopy techniques. The visible atoms are of course those at the surface of a solid. Even motions at atomic scales can be observed.

It is thus possible to identify the fundamental elements of the morphology of a surface: terraces, steps, kinks, adatoms, advacancies.

Despite the fantastic progress in surface experimentation between 1970 and 1995, surface physics relies much on theory. The theory of two-dimensional systems (e.g. surfaces) is fascinating. The transition of a surface at equilibrium from its high-temperature, rough state, to its low-temperature, smooth state, has quite unusual features, e.g. no observable specific heat singularity. The roughness of an equilibrium surface is also extraordinarily weak: a few atomic distances over several centimetres.

1.1 A high-symmetry surface observed with a microscope

In 1986, the Nobel Prize for Physics was awarded to Binnig and Rohrer for the invention of scanning tunneling microscopy (STM). This technique (Binnig & Rohrer 1987) allows the observation of the atomic structure of crystal surfaces.

The observation is easier when the orientation of the surface is close to a high-symmetry direction: (001) or (111) in the case of a cubic crystal. Such orientations are mostly used in technological applications and will generally be considered in this book. For such orientations, the microscope 'sees' (Fig. 1.1) *terraces* separated by *steps* of atomic height. These steps are not straight; they contain straight parts separated by *kinks*. On the terraces one can see surface vacancies (or *advacancies)* resulting from

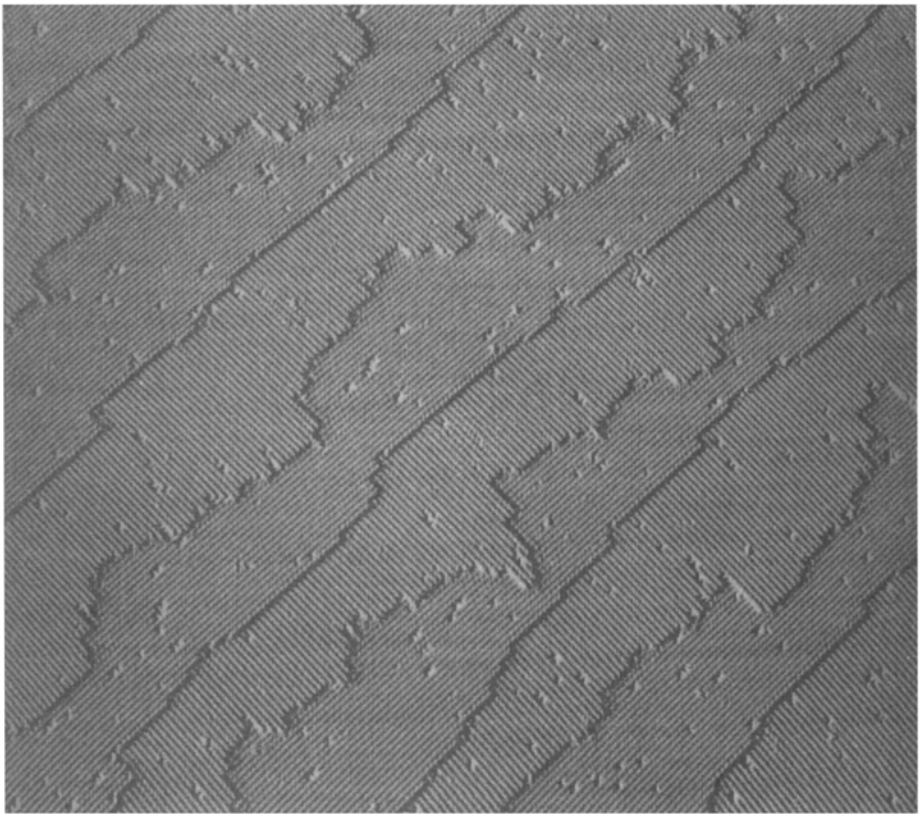

Fig. 1.1. [110] steps on a (001) vicinal silicon face. Terrace width: about 100 Å. Note the alternation of steps of different roughness, which will be explained in chapter 9. Experimental technique: scanning tunneling microscopy (STM) (Lagally *et al.* 1990, with the kind permission of the authors).

missing surface atoms. Certain features (e.g. the alternation of steps with different roughness) are special characteristics of the material which is observed, silicon in this case. They will be discussed in chapter 9.

Technical progress has been fast, and STMs exist that can now be used at very high temperatures (at present, the beginning of 1997, the limiting temperature seems to be around 1500 K). However, varying the temperature without upsetting the instrument is quite a delicate matter, and therefore the STM is not always adequate for the observation of collective motions on a surface. Indeed, the evolution of the morphology of a metal or semiconductor surface at room temperature (still the ideal temperature for most STMs) is very slow, as will be seen in chapter 8. Other methods of electron microscopy, e.g. reflection electron microscopy (REM) (Fig. 1.2) bridge this gap, and also allow the observation of larger scales. Fig. 1.2 is remarkable for the different lengthscales observed in 3 directions: the step height (perpendicular to the surface) is of order a few Ångstrøms, while the length of the steps in the image amounts to hundreds of Ångstrøms and the distance between the steps is of the order of one micron. Moreover, several steps can be seen at the same time, because the electron beam makes a very small angle with the surface

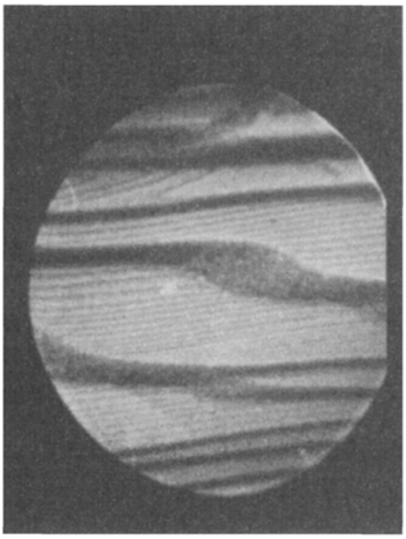

Fig. 1.2. Steps on the silicon (111) face during evaporation by Joule heating. Dark bands are macrosteps or step bunches, while thin lines are monolayer-high steps. The origin of the step bunches is discussed in chapter 9. Width: 1 μm (parallel to the steps). Depth: 35 μm (perpendicular to the steps). Experimental technique: reflection electron microscopy (Alfonso *et al.* 1992, with the kind permission of the authors).

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(grazing incidence). The steps are seen to be smoother than on Fig. 1.1. This is partly due to the different scale and surface orientation, but it is also a consequence of the fact that Fig. 1.1 shows the surface of a growing crystal, and a growing surface is far from equilibrium, as will be seen in chapters 11 to 14.

Observation of crystal growth at the atomic scale is not always easy, especially when the crystal grows from the melt or from a solution. Even in growth from the vapour, it is difficult to control the thickness of the deposited atom layer. The type of growth used in the case of Fig. 1.1 was molecular beam epitaxy (MBE). An MBE apparatus is shown in chapter 17. The principle is simple: under ultra-high vacuum conditions, atoms (single or in molecules) are sent onto the surface, where they diffuse until they meet a step where they are incorporated. These diffusing atoms are called *adatoms*. Free adatom diffusion has clearly a meaning only on a high-symmetry terrace (between steps). Adatoms are in general not easily visible by STM, either because their number is too small or because they move too quickly to be resolved by the instrument. Possible instrument-induced perturbations should also be mentioned. A scanning tunneling microscope is essentially a metal tip taken very close to the surface, from which or to which electrons can flow by tunneling. This is a rather disturbing device for the surface, and an isolated atom has a great chance to be strongly perturbed. Isolated atoms can be seen, however, by another technique called field ion microscopy (FIM) (Ehrlich & Hudda 1966, Ehrlich 1977, Wang & Ehrlich 1991). Indeed, field ion microscopy allows the observation of the motion of individual adatoms.

Adatoms are already present at equilibrium. Their equilibrium density (number of occupied sites/number of surface sites) is, according to the Gibbs formula

$$\rho = \exp(-\beta W_a) \tag{1.1}$$

Table 1.1. *Values of some typical energies (in Kelvin) for four fcc metals (Stoltze 1994)*

	Ni	Cu	Ag	Au
Adatom energy $W_a(001)$	8700 K	5900 K	4200 K	3550 K
Step energy $W_1(001)$	2200 K	1450 K	1000 K	750 K
Kink energy W_0	1800 K	1250 K	950 K	800 K
Advacancy energy (001)	8400 K	5500 K	3850 K	2900 K
Adatom energy $W_a(111)$	11650 K	8300 K	6450 K	6600 K
Cohesive energy $-W_{coh}$	51600 K	40800 K	34400 K	44000 K

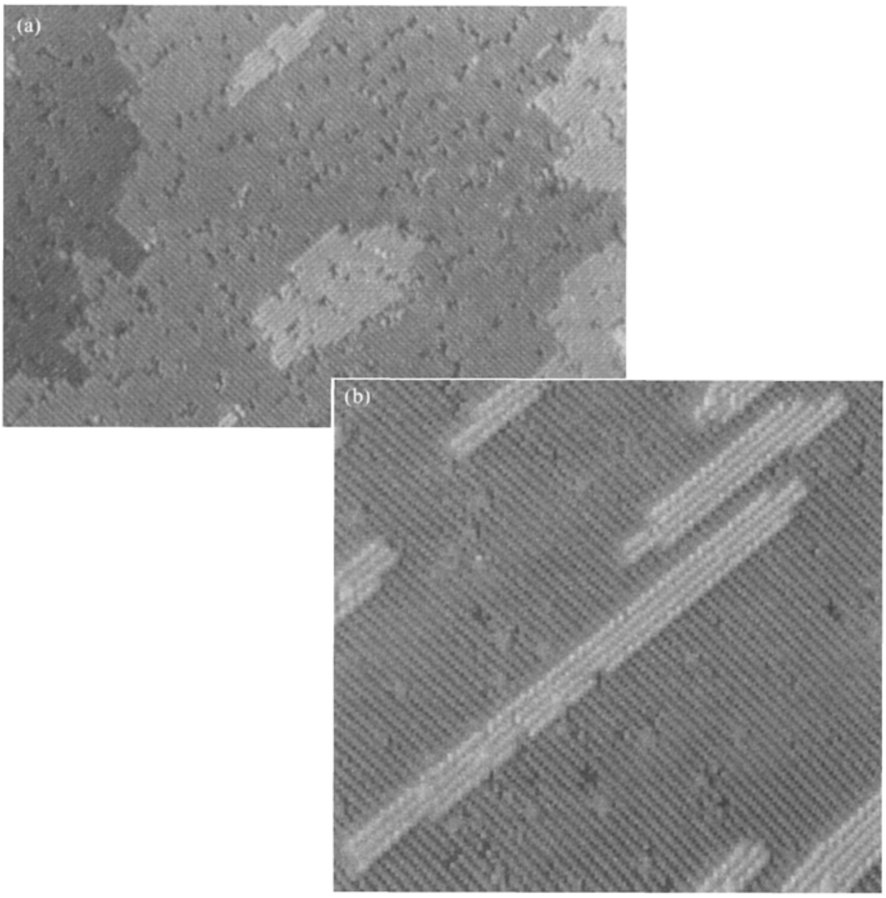

Fig. 1.3. a) The silicon (001) face after MBE growth at room temperature and annealing at 625 K. Note the terraces (or ‘islands’) and the steps. Scale: 800 × 560 Å. Experimental technique: STM (Lagally *et al.* 1990, with the kind permission of the authors). b) The silicon (001) face after MBE growth at room temperature, but without annealing. The elongated island shape indicates anisotropy in adatom sticking to steps. Scale: 400 × 400 Å. Experimental technique: STM (Lagally *et al.* 1990, with the kind permission of the authors).

where $1/\beta = k_B T$ and k_B is the Boltzmann constant. W_a is the (free) energy needed to extract an atom from a step and to make it an adatom.

It is one of the many parameters which are required for a quantitative description of surface kinetics. In this book, these parameters will be taken for granted. In principle, they can be obtained from a theory of the electronic structure, which can be *ab initio* (Gross 1990, Ruggerone *et al.* 1997) or make use of simple approximations such as ‘tight binding’, ‘em-

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bedded atom', 'effective medium'... The reader will find details in textbooks (Desjonquères & Spanjaard 1993, Lannoo & Friedel 1991, Noguera 1995) and review articles (Stoltze 1994).

Typical values of W_a/k_B according to recent model-potential calculations (Stoltze 1994) are listed in Table 1.1. According to these data, there is at room temperature, on the (111) face of nickel, about one adatom per square centimetre, which is a very low density. On the (001) face of Cu, the proportion of lattice sites occupied by adatoms is about 10^{-9} at room temperature, which is still rather low. This proportion is considerably increased on a growing crystal, as will be seen in chapter 11.

The experimental images displayed in this chapter confirm much older conjectures. We shall not review the twenty five centuries which elapsed between Democritus and the Nobel Prize of 1986, but it is worth mentioning a fundamental article by Burton, Cabrera & Frank (1951) where crystal growth was described as a motion of steps at a time where direct observation of steps (and even less of moving steps) was impossible. This article will be discussed at length in chapter 6.

What happens if the growing crystal is limited by a perfectly oriented high-symmetry surface without steps? The answer is given by Fig. 1.3: new terraces appear, at least temporarily, and therefore steps appear. In practice, a crystal surface always contains steps for two reasons: first, because it is not possible to cut it perfectly straight, and second because a crystal always contains dislocations. A screw dislocation through a

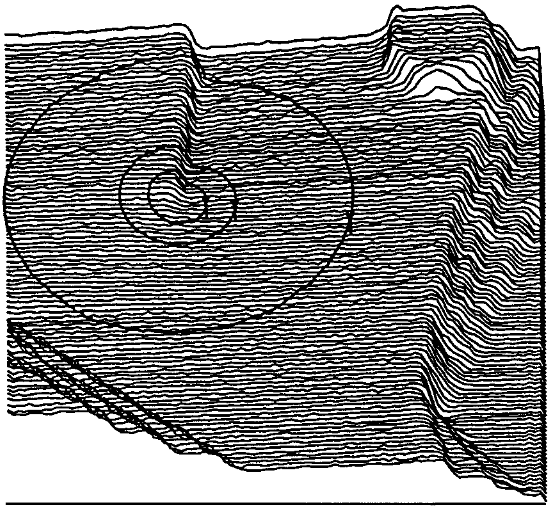

Fig. 1.4. Dislocation and steps on Ag (111) observed by STM (Wolf & Ibach 1991, with the kind permission of the authors.)

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surface is necessarily, for geometric reasons, the origin of a step (Fig. 1.4). However, dislocation-free surfaces on macroscopic scales can nowadays be grown for certain materials, e.g. the technologically essential element silicon.

1.2 *In situ* microscopy and diffraction

Now that we have a surface microscope, we would like to look at the surface of a growing crystal as it grows–or, as the jargon demands, *in situ*. It is not that easy, however. On one hand, it is hard to imagine introducing any microscope into a liquid metal or silicon melt! On the other, even though the use of a microscope is in principle easier during vapour phase or ultra-high vacuum growth, each different technique has some specific limitations. Reflection electron microscopy can be used at any temperature, but the images suffer from the strong foreshortening effect seen in Fig. 1.2, which limits the ability of seeing small details. Low-energy electron microscopy (LEEM) does not have this problem, and it has been used for *in situ* studies of growth (see Bauer 1992 for a review), but its resolution is poor (5 to 15 nm) compared to STM. The latter is limited to not-too-high temperatures by technical difficulties which will be certainly overcome in the future, and still suffers from a long–but steadily decreasing–image acquisition time. Some *in situ* observation of growth has started showing up in the literature (Voigtländer & Zinner 1993).

More appropriate for *in situ* observations than microscopy is still diffraction, i.e. scattering of electrons, X-rays or atoms. In a scattering or diffraction experiment (we shall use both words with essentially the same meaning), one measures the scattered radiation as a function of the scattering angle. The analysis as a function of the energy is essential in certain cases, but we shall not care very much about it in this book. The essential difference between microscopy and diffraction is that the diffractionist works in reciprocal space rather than in real space. For a good, three-dimensional crystal, the diffraction spectrum can be interpreted by any student. In the case of a reasonably smooth crystal surface, i.e. a two-dimensional object, the task is already harder. And if the number of imperfections becomes very large, the interpretation is very difficult. On the other hand, pictures from a microscope are understandable (after some image processing, sure...) by the layman, and can in principle be obtained even for a non-crystalline material.

1.3 Step free energy and thermal roughness of a surface

At zero temperature, a surface at equilibrium should contain no step. At low temperature, there are a few adatoms as seen above; there are fewer pairs of adatoms, whose number (or better, whose density) may

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be obtained by a Gibbs formula similar to (1.1); and smaller yet is the density of larger clusters. Atom clusters are closed terraces bounded by steps. The step density (total step length per unit surface) increases with temperature.

This increase is not easily seen directly by microscopy. Indeed, most of microscopic methods work best at low temperature, when the surface does not easily attain thermal equilibrium. The atom scattering or X-ray diffraction signal does exhibit a dramatic broadening when temperature is increased (Fig. 1.5). Above some temperature, the lineshape, which is lorentzian at low temperature, undergoes a qualitative change. One can for instance measure the 'specular' reflection, i.e. that whose reflection angle almost equals the incidence angle (*speculum* is the Latin for mirror).

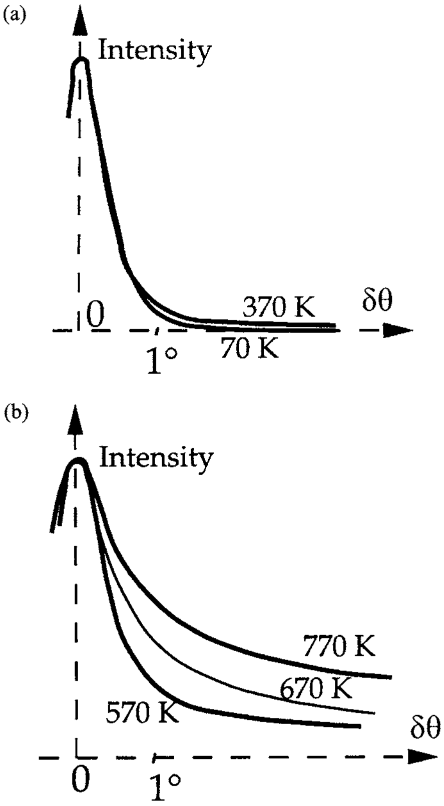

Fig. 1.5. Atom scattering lineshape at temperatures (a) below and (b) above T_R =380 K in Cu(115), after Fabre *et al.* (1987b). The reflected intensity is plotted vs. the deviation $\delta\theta$ with respect to the reflection angle corresponding to the ideally smooth surface.

The specular peak (as well as the Bragg peaks) is narrow for a smooth surface while a rough surface scatters radiation in all directions.

This type of experiment is a quantitative version of everyday observation. Galileo (1632) was perhaps not the first who noticed the importance of surface roughness in light scattering, but he was presumably the first one who realized that light was scattered rather than lost. His problem was to understand the brightness of the moon, which he compared to a wall scattering sunlight:

> *You see the difference between the reflections occuring on the respective surfaces, that of the wall and that of the mirror: ... Look how the reflection from the wall scatters to all parts of the opposite wall, while that from the mirror goes to a single part, not larger than the mirror itself... If you want to understand all that, you should notice that, for a surface, to be rough means the same thing as to consist of innumerable small surfaces of innumerable orientations, and it necessarily occurs that, among them, many have the appropriate orientation to direct the reflected beams to this place, and many to that place.*

The interpretation of diffraction patterns from a hot surface is difficult (Blatter 1984, Levi 1984, Armand & Manson 1988) because the effect of atomic vibrations adds to roughness to broaden the reflected beam. It is however clear, from a quantitative analysis, that the total step length is greatly increased by heating.

The reason is basically the following. Even if the step energy per unit length, W_1, does not change much, its entropy increases, so that the free energy decreases. In order to calculate it, we consider (Fig. 1.6) on the (001)

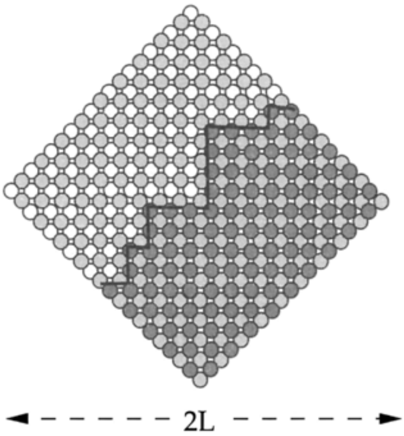

Fig. 1.6. A step on a surface with a square symmetry, e.g. the (001) face of an fcc metal. For this orientation, the line tension is given by (1.2).

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face of a cubic crystal a zig-zag step, whose average direction makes an angle of 45° with bond directions. This step orientation is chosen because it allows a simple, though approximate, calculation. The only configurations which will be considered are those which result from random walks going from the left to the right, each step of the random walker being parallel to a lattice bond, and backward steps being forbidden. This definition may be complicated, but what it means is clearly suggested by the figure. If the width of the system in the direction of the walk is uniformly equal to the bond length multiplied by $L\sqrt{2}$, all configurations have the same energy $2LW_1$. Since there are 2^{2L} configurations, the entropy is $2L \ln 2$ and the free energy per bond is

$$\gamma = W_1 - k_B T \ln 2 \,. \tag{1.2}$$

The free energy per unit length γ/a is called the line tension of steps. Since a, the lattice parameter, is generally chosen as the length unit in this book, the term line tension will be often employed for γ itself.

When γ is positive, one has to provide mechanical work to introduce a step into the surface. If the total step free energy $L\gamma$ becomes negative, thermodynamics tells us that one should provide mechanical work to remove steps from the surface. Thus, equation (1.2) tells us that the surface undergoes a transition at a temperature T_R approximately given by

$$T_R \approx \frac{W_1}{k_B \ln 2} \,. \tag{1.3}$$

This transition is called the roughening transition.

1.4 The roughening transition

As seen above, the roughening transition temperature may be defined as the temperature at which the line tension of steps vanishes. According to the experiment (Fig. 1.7) the line tension does vanish at some temperature. The linear temperature dependence predicted by formula (1.2) is in pretty good agreement with experimental observation, at least far from T_R. Near T_R, the experimental curve bends away from the straight line: one can wonder whether it is an instrumental effect or a fundamental one. As will be seen in the next section, it is a fundamental effect. But before discussing that, we would like to make three remarks.

1) The roughening transition temperature depends on the surface orientation, i.e. it is different for a (111) and for a (1,1,19) surface. This point will be addressed in section 1.7.