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Wedding cakes and pointed caps: Structure formation on platinum

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Investigating the mechanisms of layer growth is a central concern of modern surface physics. Motivated by the prospect of producing technologically relevant layers by intervening in the growth process, the field also offers fascinating insights into self-organization far from thermal equilibrium. In this article, we report on new experiments on the growth of platinum on platinum, in which we were able to observe the formation of regular pyramidal structures [1]. The results can be clearly explained by analyzing the interaction of random atomic processes in more detail.

Structure formation during layer growth is a phenomenon that occurs under almost all conditions.
of the layer deposition
is respected. This is a particularly simple situation - but one that is im
The most common form - which is still surprisingly rich - is homoepitaxy, the growth of layers on a crystalline substrate of the same material. In this case, no internal structures (e.g. grains) are formed, and the
Structure formation is limited to the surface of the growing layer.

An example is shown in the scanning tunneling microscope image of a thin homoepitaxial layer on the R(111) surface in Fig. 1. This layer was separated from a surrounding Pt vapour by statically impinging R atoms. It consists of "mountains" of similar size and height, which are clearly separated by deep trenches.
Fig. 2 provides an insight into the formation of such mountains, showing layers of successively increasing thickness that are under otherwise identical conditions

were deposited. At first, in the initial stage of layer deposition, in-

The crystals are monoatomic in height (Fig. 2a), which are somewhat irregularly triangular in shape and whose step edges run along distinct directions of the crystal surface (see Fig. 3a).
These islands grow laterally, melt and leave holes in the coalesced layer. At the same time, new islands germinate. After just a few deposited layers, it can be seen that at most one new island forms on an existing island (Fig. 2b), and that the rate of lateral coalescence lags behind that of germination, i.e. the layer becomes rough. After about ten atomic layers have been deposited, clearly distinguishable mountains have formed on the surface, which can be recognized by the germination of new islands on the surface.
grow upwards from their summit germinated islands on the mountain plateau (Fig. 2c). The newly peaks now have stepped edges, formed which are located along the (110) directions of the cri-
stalline substrate are oriented even more regularly than
this was the case at the beginning of the layer growth. The comparison of Fig. 2c with Fig. 2d also shows that the structure formation process is essentially completed after the first ten deposited monolayers. The further layer deposition only causes a growth of the mountains perpendicular to the base (increase in roughness) and a deepening of the trenches burning them. The lateral

Fig. 1:
The Wachsium of Flatin on Pla- tin creates mountain structures that are separated by deep trenches. Here is a micrograph of one of the Pt{111}-Surface, after 650 Ä or 300 monolayers of platinum at 440 K were deposited on it.
Image size 4700 Ä x 4700 Ä.

The extent of the mountains, on the other hand, no longer changes; there is no coarsening of the growing layer.

The "minimal" model

To understand this experi- We first look at the processes involved in waxing of the first monolayer. Atoms of thermal energy are released from the vapor with an average de-

position rate F (in monolayers per Second or identical thereto: in atoms per lattice site and second) are randomly adsorbed onto lattice sites. These *adatoms* are mobile and can switch to a neighboring lattice site with an average hopping frequency r due to thermal excitations from the heat bath of the crystal. In the simplest case, nucleation occurs when two mobile adatoms randomly move to neighboring lattice sites and form a dinner.

Priv.-Doz. Dr. Thomas Michely, I. Physiological Institute, RWTH Aachen University, Dr. MatthiasKulff Continental-Teves, AG, ß044l Franhfort/Niairi, Pro1. Dr. Joachim grag "na n . rau" Poliö, department Physih, University GH Essen, 45117 Essen

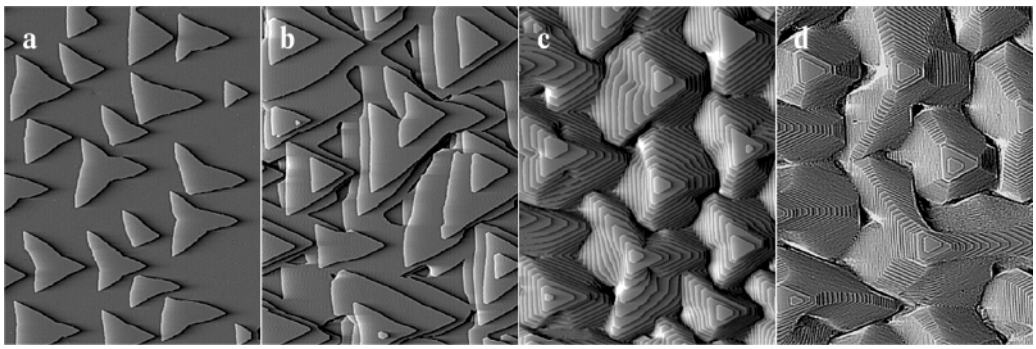

Fig. 2:
After around 10 monolayers of 'ML}, the **5trukiurliI-**dation alclosed: Plaiins structures after deposition o f aJ 0.5 ML, ßJ 3 ML, cJ 12 ML andß d) 90 ML under otherwise identical conditions as in All. 1. the topography appears in this representation. phie sireifend from linhs beleuchtei. All visible steps are of monoatomic height. BiId size 2600 Ä x 5450 Ä

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Such dimers grow into islands by the addition of further adatoms, as shown in Fig. 2a. Elementary nucleation theory shows that the mean island distance *L* (from center to center) increases with

$$L \; i \; vi \; F) \; "^{6}. \qquad (1)$$

scaled [2].

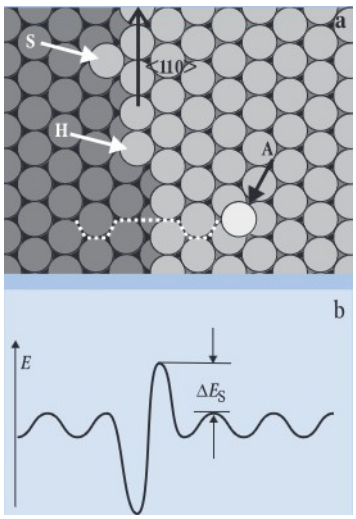

Fig. 5:
ß- a} Top view of **a spherical model of a surface-centered** {1ll}- **surface with step, semi-crystalline layer {H), Siufen-adatom (S) und Adatom (A)**
ß- 1) Potential energy of the atomization of the **path indicated** in a}.

The decisive question for the three-dimensional structure formation is now: What happens to the particles that are deposited in/on the islands? Figure 3a shows a spherical model of a surface with an adatom and a step. Before the adatom can be built into the step, it must jump down over the edge of the step. In doing so, it goes through a configuration of reduced coordination, which leads to increased potential energy. When jumping over the edge of the step

Istenl:TheZeno-Bnekt

If mass transport between **different** atomic layers is completely suppressed, only those atoms that end up in the fifth layer contribute to the growth of this layer. The number of these atoms is proportional to the uncovered fraction of layer *h* -1. Therefore, the coverage ß$ of the ii-th layer grows according to the linear equation

$$d\,\theta_h/dt = F(\theta_{h-1} - \theta_h). \qquad (\text{'}$$

As can easily be checked by induction via ii, the solution with the boundary condition dp = 1 and the initial condition dig= 0 is

$$\sum_{n=0}^{n-1} \frac{h^n}{!}$$

edge, an additional energy barrier, the *S* fM *fenran dbarrier* ÖEs. must be overcome (Fig. 3b). At a given temperature T, the probability that the jump into the abyss will succeed is equal to *s* - e*"S/#tT. The effective

Jump rate r' = s- for jumps between different layers is therefore smaller than the jump frequency r within a layer. This effect was discovered experimentally by Ehrlich and Hudda over thirty years ago [5]; however, its eminent importance for layer growth has only been clearly recognized in recent years [4].

In the sense of a minimal modeling, we assume that l the column boundary barrier is infinitely high. is, therefore - 0 [5]. Adatoms *af2/* In- selves can then be used at all.
not leave the island. As soon as two atoms have been deposited on an island, a new nucleus is formed after a short time, which grows exclusively through further atoms deposited *on* the island. The formation of *two* nuclei on one island is extremely unlikely, as one nucleus already empties an area of the island.
Largest L^2 effective, as the germination in the first layer proves. The result is a morphology of upwardly tapering island stacks, or "wedding cakes", at the top of which there is an ato- marous dinner instead of the marzipan wedding couple. The mountain formation (or wedding cake bakery) takes place in a monolayer cycle according to the following simple sequence: germination on an island -' growth of the germ to the island -' renewed germination on this island.

T h e first layer never closes completely, because d = 1-a ' is always less than 1. Elkinani and Villain [9] have coined the term "zero effect" for this, in reference to the paradox of Achilles and the tortoise: The greater the coverage of the first layer, the smaller the probability that another atom will stray onto the substrate, and the slower the layer grows. The Zeno-B effect explains the formation o f canyons between the mountains on the platinum surface.
Due to the finite size of the a t o e , **the** first **layer** will close at some point, namely when the uncovered areas at the bottom

In this model, the spatial distribution of the mountains is already definitively determined by the islands of the first monolayer; in particular, the mean distance 2 between the mountains is equal to the distance L between the islands, independent of the layer thickness. p
There is practically no mass transportation between the various mountains. ¿
sent transportation. The area of the *h* -th island of a stack, in relation to the x
base area *A* L² of the stack, is therefore jus equal to the
cover *8g* of the *h* -th monolayer.
The analytical expression for *85* as B function of the number *h* -- *ht* of de- poned monolayers is derived in Ka-
j sten 1, equation (ii). go
The shape r(h) or *h ir)* of a radially by Cochran
symmetrical mountain with base *A* then simply follows
from the relation er(h)² = A *8* . Thus resulted in the pointed cap profile shown as a dotted line in Fig. 4. The difference *P[h1 -* *8p - 8 +* is the uncovered part of the h- th layer. This is equal to the Probability, data of a randomly selected point on the surface is in the h-th position, i.e. the layer at this point is just France, Wiley Online Libr 3

h layers is thick. According to equation (ii) *P(h)* is a Poisson distribution with mean value k. Since the standard deviation of a Poisson distribution equal to the square root of its mean value, the standard deviation of a the roughness w = *(h - (k)² j"'* of the layer according to the simple law o - (ii)!'*. Term is Condition (https://onlinelibrary.wiley.com/terms-an

Good match with the experiment

To what extent do the predictions of the minimal model correspond to the experimental results? To analyze the experiments, the layer roughness and the mean uphill distance d as a function of the mean layer height d thickness /i is determined. Fig. 5 shows g
the results of an extended series of measurements (open squares) are plotted together with the model predictions (dotted lines). ine Library for rul
Apart from an initial phase the agreement with the OA
b model is excellent: the roughness a increases precisely with (/i) "2, rticles are governed
and the uphill distance Z does not change within the measuring accuracy. In the range up to about three
Monolayer doubles all 4 th

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however, the structural grottoes and the

ß5(f)=1- e*'

(')

with /i= *Ft*. From this follows astonishingly-

of the canyons are only one atom in diameter, i.e. at a Layer thickness of the order of magnitude In J.

Roughness development falls short of expectations. On these initial deviations

We will come back to this later. In Fig. 4, the theoretical peak cap profile of a mountain (dotted line) is compared with an average experimental mountain profile (solid line) after a layer thickness of 500 monolayers. Here, too, there is a very good qualitative and quantitative match: the two curves almost coincide except for the summit area of the mountains. In particular, both theoretically and experimentally

narrow and deep trenches between the mountains (see also Box 1), and at the foot of the mountains a

Area of negative curvature, which merges into an area of positive curvature towards the top of the mountain. Only in the summit area, instead of a sharp peak cap, is there an experimental

The summit plateau can be clearly seen in Fig. 2d.

The striking agreement of the observations with the infinite barrier model makes the analysis of the discrepancies all the more important. As we will show in the following, all discrepancies can be traced back to the fact that the step boundary barrier is firstly coarse, but not infinitely high, and secondly that it shows an unexpected dependence on the deposited layer thickness, i.e. that it changes in the course of growth.

Wie entstehen die Gipfel-terrassen?

The cut-off pointed caps can be clearly understood as the poles of the step edge barrier $_{UBS, which}$ in reality is only finitely high. that an adatom not un-finitely often, but only 1/P - times [6]. This is insignificant for the adatoms on the flanks of the mountains, as they reach the upward step edge after a few refections and remain bound there. For the summit terrace, however, there is a qualitative difference: Here, the final reßection probability $_{PS}$ leads to a finite residence time. time i - $_{1/PS}$ of the adatoin. Becomes during this time no second particle is deposited, the adatom leaves the terrace and is built one layer deeper into the step edge. The probability of the deposition of a second atom during the residence time of the first atom (and thus the nucleation time) is increased.

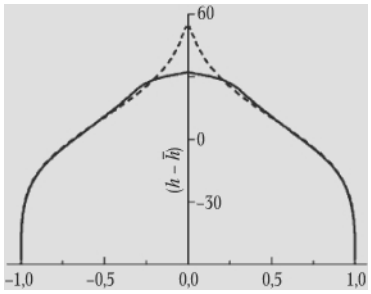

Fig. 4:
Heave profile of a mountain after deposition
on of 300 HL. Pinned line:
retishe profile at infinitely high him-**edge barrier; durehgeaogene line: milHer experimental profile,**
determined by analyzing the distribution of **individual mountains, normalization and 3division over approximately aebn mountains.**

The "tlberschwinger" of the experimental curve compared to the theoretical curve is easily explained by the downward transport of material from the gypsum rock terrace before nucleation.

Die Höhe der Stufenrandbarriere hiingi an der schichidiw a

So far, it has been implicitly assumed that the step boundary barrier is a constant variable during growth and independent of the island shape. In reality

However, the height of the barrier depends on the *local* atomic confiu-ation of the step. Experiments

and simulations show that for steps on Pt(111) the barrier for the path over a close-packed step edge as in Fig. 3a is of the order of 0.2 - 0.3 eV,

probability) is a strong increasing function of the island disappears (equation (iii) in Box 2). morphology changes, as edges from monolayer to monolayer. gypsum nolayer - must change during the the diameter f of the summit terraces. terraces must change during the growth process. shows during the deposition of a mono the island of exactly one nucleus. formation event occurs. This monoconditions leads to the estimation of the first ten monoconditions leads to the increasingly step edges

$$f - (r'/\ ''\ . \qquad (2)$$

Together with GI. (1) it has been possible about 1 °/o with succeeded in reducing the two length- easy to understand in the context of the inini- scales of layer morphology model. context of the inini- scales of layer morphology model. the mean island distance L and the coarseness f of the summit terraces - structure- with the microscopic paraine- increasing F, r and r' of the growth process. the flan- ces in quantitative relation to move closer together. For our platinum layers the exact evaluation leads to a proportional to the step edge barrier of about decreases. 0.25 eV. The in the height profile unmit- attached to the step and is located below the summit terraces. Atoin therefore has more time,

while for the way down to of a semi-crystalline layer almost decreases [7, 8]. Thus, if the layer the atomic structure of the layered edges - especially that of the terraces - during the growth of the diameter f of the summit barrier. In fact, Fig. 2 a drastic change in the position on Step edge structure: During the deposition of the first ten The deposition of the better alignment of the

along the (110) directions, the concentration of the semi-crystal from about 20 ß/o to from. This is Because of the as (fi)"^{2} increasing roughness with constant the mountains are always ler. The step edges on The step edges at the flanks thus and the growth rate, of the step edges, which is to the terrace width, Any atoin that is

Z¢aaten 2: IEefmbitdung aa£ Gipfeftexzaaeen

The probability that 8 while the stay of an adatnm on summit terrace a second there is deposited is given by the the mean residence time z of the adatnm to the mean time interval df between two deposit events. The rate l/r at which the adatom misses the island, sets the ticket Pg that it is located at a stu-fenrandplats, and the rate p' = Pty with which it jumps down. URtTf forms a nucleus. The expression for the probability of stay8 therefore equal to 1/(nJ), which finally (which confirms a more precise calculation) is valid for a circular island, whose of radius r is atom distances: Pp= the 2w/(W) - Z/r, and snwith r= r/2y'. Pfor the same genetics is df - I/(Pol), ratio of so that the sought-after germination probability to

$$\tau/\Delta t = \pi Fr^3/2v' \qquad (iii)$$

results. The diameter / the summit of terrace is determined by the porde- lity ;-pg, that the nN atoms that during the growth of a Mnno-the average of a spatially hOmO- nes (iii) is

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leads to the estimate (Z).

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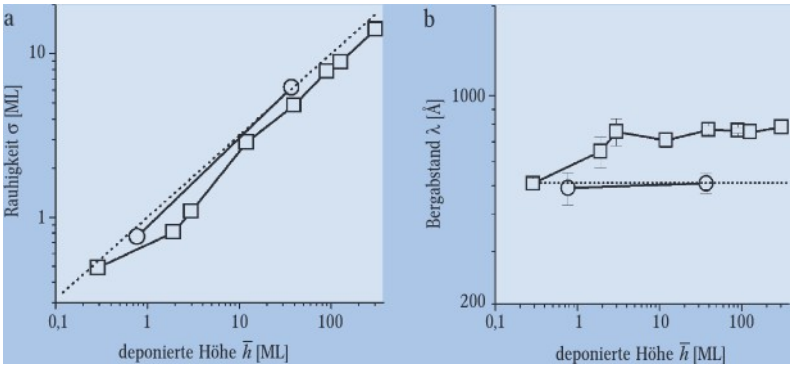

Fig. 5:
• a} Surface roughnessp and
• b) **mean downhill level** d as a function of the milHer deposited height R Ak h2aB for o lsw. 4, the height-height correlation function G(rJ -tOt-'-*'t9--o-M}) at the points G{0J or Gt4f2J = 0 for the different Values of 6 evaluated. The oHen The squares correspond to the deposition conditions as in Figs. 1, 2 and 4. The **upper i£reise correspond to Alscfieidnng** in a carbon monoxide partial pressure of ppp= 1.9 x10 ' mbar. The dashed line in aJ corresponds to the model prediction p=(6)^' and in 1 J to the prediction tpy ppp$t.

to find an optimal installation position and the steps become smoother.

The gradually increasing step boundary barrier now directly explains the deviations from the minimum model in the initial phase of growth. Initially, there is still a considerable transport of material down from the islands, which pushes the roughness below the predicted value (fi)"^{2} and ensures increased melting of islands without a new nucleus having formed on each island beforehand. As a result, the number of summit terraces is reduced in the initial phase and the structural roughness 2 increases, as shown in Fig. Sb.

Independent support for this argument is provided by wax experiments in the presence of an adsorbing impurity gas. Adsorbed carbon monoxide is highly mobile at 440 K on Pt(111) and adheres preferentially to step edges. There it impedes the transport of atoms down the step, thus it increases the step boundary barrier [7]. In a carbon monoxide partial pressure that is sufficient to always c o v e r all step atoms with CO molecules, the barrier is high from the start of growth and the initial deviations in roughness and structure size from the minimum model should disappear. The quantitative evaluation of the CO experiments in Fig. 5 confirms this picture.

Outlook

The example presented here impressively demonstrates the detailed understanding of structure formation during layer growth that is possible today on the basis of simple models. The basic principles outlined here can be used to analyze a variety of growth processes. On the other hand, it should not be concealed that most experimental systems are much more complex. Among the many unsolved problems, one of the most exciting i s t o g a i n an insight into the atomistic processes involved in the in ner structure formation in thin films. For example, how is the texture of the polycrystalline layer formed during deposition on ainorphous substrates, and
Which elementary processes are responsible for
responsible for the frequently observed columnar morphology?

Acknowledgments

T. M. and M. K. would like to thank Pavel Sinilauer and George Coinsa for their collaboration on the experimental part of the results presented here. Our work was supported by the DFG through a Heisenberg fellowship (T. M.) and within the framework of the SFB 237 "Disorder and Large Fluctuations" (J. K.). P. P. would like to thank the Alexander von Humboldt Foundation for granting a research fellowship.

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