From Wulff Kaishew' theorem to nanodots

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Abstract
This paper is devoted to professor R.Kaishew' 100th birthday ceremony. It intends to illustrate his theorem especially when some inherent simplifying conditions are released (e.g amorphous substrate, stress free system). It is shown that some new insight was brought for the better understanding of present day arrays epitaxial dots, which are said to be promising tools in solid-state electronics.

Introduction

The paper will be divided in six parts:
1/ We first recall the somewhat long and tortuous genesis of the Wulff' theorem which at the end, clearly concerns the equilibrium shape (ES) of a freestanding crystal A.
2/ Kaishew' important achievement was to predict the ES of a crystal A sitting on a planar substrate B restricted to be amorphous and the system being stress-free.
3/ When releasing this limitation, allowing the substrate B to be crystalline too, epitaxial orientations may install. For coherent epitaxy high stress and strain appear not only in the contact area but spread out in A and B. Elastic energy has to enter in the formulation of the free energy, and has to be minimized (elastic relaxation) as well as the shape. The new theorem shows that ES is deeply modified by the relaxed elastic energy.
4/ Upon some critical size of the deposit crystal the stored elastic energy becoming too expensive, introduction of interfacial dislocations makes to release partially this energy par saccade. Consecutively, the ES retrogrades, at its proper rate, at each dislocation entrance.
5/ Due to (3) and (4) a dot A pilots, outside its contact area, a zone of nearly the same area where the non covered substrate B bears stress σ_1 and strain ε_1. This is a kind of "antenna" that enables each dot A_1 to detect at distance other stress-strain fields of the substrate.

6/ To this “2D communication” there has been imagined and realized its equivalent of “3D communication”. Defects A are buried in B close beneath the surface. The stress-strain field of the defects $\sigma \sim \varepsilon$, spreads at the free B’ surface where material dots A' preferentially “choose” to grow epitaxially at loci where the $\varepsilon_{B'}$ map has the smallest misfit with these A' dots.

1. Towards the Wulff theorem:

At the end of the 19th century, Gibbs [1] then Curie [2], interested in equilibrium capillarity, went to anisotropic crystals and their well-known polyhedral shapes. They showed that the total free surface energy $\Phi=\sum_i \gamma_i S_i$ has to be minimal for crystal polyedra at constant volume $V=\frac{1}{3}\sum_i h_i S_i$ when the area S_i are varied arbitrarily. Still at that time, very fond of variational calculus, Gibbs [1] went unfortunately not further to solve the general problem. Curie gave an exact solution but based only on some explicit crystallographic form combinations. He found, in such case, that the central distances h_i to the surfaces S_i of the stable equilibrium shape (ES) have to be proportional to the γ_i :

$$\gamma_1/h_1=\gamma_2/h_2=....\gamma_i/h_i=Cte \qquad \textbf{(1)}$$

Curie [2] called them capillarity constants but gave the same definition as that of Gibbs: specific surface free energy of an incompressible system (zero strain)[1]. The constant of proportionality however was not precised.
Wulff ‘s (1901) famous paper [5], quoted as Wulff theorem, has in fact not received a right demonstration (p. 520) as was shown in (1914) by

[1] It is known that Gibbs introduced the two distinct intrinsic properties of surfaces of solids γ_i precisely the above specific surface free energy concerning the work of creation of a surface i and s_i describing the in-plane state of stress of a planar solid surface in equilibrium with its environment. These surface forces s_i work when the system is mechanical deformed. For the 80th birthday paper [3], we gave some working routes; for closer inside see [4].

Liebmann [6] whose critic however was for many years overlooked. Instead giving arbitrary variations to the S_i and h_i, Wulff considered only those who lead to self-similar polyedra by writing $\Phi \propto \sum_i \gamma_i h_i^2$, $V \propto \sum_i h_i^3$. Since $d\Phi \propto \sum_i \gamma_i h_i \, dh_i$, $dV \propto \sum_i h_i \, dh_i$ when equating both to zero we cannot conclude the γ_i / h_i proportionality (1) as done by Wulff. Liebmann [6] gave a correct demonstration by omitting this initial restriction and performed arbitrarily variations of h_i to faces i as well of S_i to these faces. Up to the first order this gives: $dV = \frac{1}{3}\sum_i S_i \, dh_i + \frac{1}{3}\sum_i h_i \, dS_i$. This volume change being calculated differently up to the same order:

$$dV = \sum_i S_i \, dh_i = \frac{1}{2}\sum_i h_i \, dS_i \qquad \textbf{(2)}$$

Variational calculus with conditional ($dV = 0$), minimum reads $\sum_i \left(\gamma_i - \frac{\lambda}{2} h_i \right) dS_i = 0$ where the arbitrary variations have to be $dS_i \neq 0$ so that one has a set of i equations and therefore there is :

$$\gamma_1 / h_1 = \gamma_2 / h_2 = ... = \gamma_i / h_i = \lambda / 2 \qquad \textbf{(3)}$$

that means the Curie result (1).

Notice that relations (1) to (3) mean self similarity ES crystals as long as the γ_i are size independent.This is a consequence of the correct demonstration of Wulff's theorem and not a premise. Furthermore, this self similarity (1-3) became helpful

1. As the now so-called Wulff's construction of the ES (at the scale $\lambda/2$) when knowing the γ_i in all directions $\vec{h}_i / |\vec{h}_i|$ of face normals
2. To determine the surface energy anisotropy by measuring the central distances on ES crystal then by means of the relations $\gamma_{i \neq 1} / \gamma_1$.

However this famous paper [5] contains further very misleading matters bringing great trouble for a long time. Does not the title announce "About the question of velocity of growth of crystal faces" though its real positive content concerns ES crystals, such ones of zero growth velocity ? Manipulating $\gamma_i / h_i = Cte$, Wulff strengthened his conviction: growth

velocities v_i have to be proportional to γ_i since the v_i are nothing else than dh_i/dt per unit time. His faith found confirmation by the very known fact that crystalline faces of high velocities disappear while those of low velocity remain on the crystal (growth) shape satisfying by the way the minimal surface energy. Such farrago made great damage to the field for a long time.

Only in the year 1943, M. von Laue [7] was appreciative of Liebmann' demonstration. He gave himself a demonstration based on the independent variables h_i instead of S_i . In other words, he used the first of relations (2), considering it as an exact differential $\partial S_i/\partial h_k = \partial S_k/\partial h_i$, he applied (p 129) Euler's theorem of homogeneous functions, then applying Lagrange multiplier calculus, leading to (1) (3), he could identify λ with

$$\lambda/2 = \Phi_{ext}/3V \qquad \textbf{(4)}$$

In the same series of papers, I.N.Stranski [8], following Volmer's book, derived Wulff's theorem directly from thermodynamics by transferring $n = V/v_c$ molecules (of volume v_c) from the ambient phase, at constant thermodynamic supersaturation $\Delta\mu = kT\ln(P/P_\infty)$ to the crystal. The constant and Wulff's theorem then becomes:

$$\lambda/2 = \Delta\mu/2v_c = \gamma_1/h_1 = \gamma_2/h_2 = \gamma_i/h_i \qquad \textbf{(5)}$$

Stranski called (5) the generalized Gibbs-Thomson equation by analogy with liquids where for crystals the γ_i are now anisotropic. Let's note that we do not at all mention here the atomistic treatment of surface energies and ES derivations where Stranski and R.Kaishew have been so much active nor the papers of C.Herring, W.W. Mullins and many others authors where e.g. the very fruitful techniques of γ-plots have been introduced. The same can be said for the experimental works associated with such matter and where specific ES have been analysed. We have reviewed this in [9].

2. Kaishew's theorem

Free standing ES crystals are not easy to produce[2]. As for droplets, this can however be done more easily when the crystals are lying on an inert flat and horizontal surface as glass, plastic or some crystalline material[3].
R.Kaishew considered [12-14] the proximity effect of deposit A on substrate B in its simplest form. The substrate is supposed to be amorphous so that only the crystallographic nature of the crystal face of A brought in contact has to be considered. Its azimuthal orientation is of no matter since all of them would be equivalent. The free energy change for creating a crystal A of V'/v_c molecules from an infinite reservoir of molecules of constant supersaturation $\Delta\mu$ with a shape of S_i' free faces and contacting area $S_{AB}=S_B$ (see Fig 1) of interfacial free energy γ_{AB} created at the expense of γ_B is: $\Delta F=-\Delta\mu V'/v_c+\sum_{i\neq AB}\gamma_i S_i'+(\gamma_{AB}-\gamma_B)S_{AB}$
Supposing, as in Fig. 1a,b,c that the opposite equivalent of the summit of face $i=1$ of A comes in contact with B, Dupré' relation states $\gamma_{AB}=\gamma_A+\gamma_B-\beta_{AB}$ where β_{AB} is the specific adhesion free energy of the face $i=1$ of A on B. The quantity $\gamma_{AB}-\gamma_B$ in ΔF can be thus replaced by $\gamma_A-\beta_{AB}$. Using furthermore the basis areas S_i' of the pyramids as independent variables, we use (2) so that the emerging volume V' change reads: $dV'=\frac{1}{2}\sum_{i\neq AB}h_i\,dS_i'+\frac{1}{2}h_{AB}dS_{AB}$ where the distance h_{AB} is that of the common pyramid summits O to the interface AB. It is taken negative if located inside the substrate S but positive if located in A. The free energy change thus reads:
$d\Delta F=-\frac{\Delta\mu}{2v_c}\left[\sum_{i\neq AB}h_i\,dS_i+h_{AB}dS_{AB}\right]+\sum_{i\neq AB}\gamma_i\,dS_i+(\gamma_A-\beta_{AB})dS_{AB}=0$. Thus there is:

$$\lambda=\frac{\Delta\mu}{2v_c}=\frac{\gamma_i}{h_i}\qquad \text{for } dS_i'\neq 0 \text{ and } i\neq AB \qquad \textbf{(6)}$$ and

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[2] Closed environment among other conditions are necessary to install for stable equilibrium at supersaturation (see [9] p 84-98 and p 179-199).
[3] Gravity effects are harmless and can be neglected for usual densities and sizes smaller than 0.3-0.5 mm [10-11].

$$\lambda=\frac{\Delta\mu}{2v_c}=\frac{\gamma_A-\beta_{AB}}{h_{AB}}\equiv\frac{2\gamma_A-\beta_{AB}}{H} \quad \text{for } dS_{AB}\neq 0 \qquad \textbf{(7)}$$

Notice that $H=h_A+h_{AB}$ is the height of the emerging crystal A above the substrate surface B measured to the summital face A. Kaishew's theorem (7) thus says that the emerging ES is that one of the Wulff's theorem (6) but truncated by the substrate at H.

In Fig 1 are drawn the different situations for different sizes λ of the crystal A and different adhesion energies β_{AB} with respect to the surface free energy γ_A.

For a given size, when $\beta_{AB}<\gamma_A$ and $\beta_{AB}\to 0$ (Fig. 1b and 1a) the truncation decreases and tends towards zero. The other extremum (Fig. 1d) is when $\beta_{AB}\to 2\gamma_A$ so that the emerging part of A tends to zero, $H\to 0$. By analogy with a liquid drop, where $\gamma_i=cte$ is isotropic, Fig 1a corresponds to a free sphere, Fig. 1b to an incomplete wetting of the surface with a wetting angle $\pi/2<\alpha<\pi$ and Fig. 1c to half a drop sitting on its underlying substrate ($\alpha=\pi/2$ or $\beta_{AB}=\gamma_A$). Fig. 1d corresponds to $\beta_{AB}<2\gamma_A$ and $\beta_{AB}\to 2\gamma_A$ that means to the full wetting case $\alpha\to 0$ [4]. In fact one is not limited to this case but may consider $\beta_{AB}>2\gamma_A$ so that real 2D solid (or liquid) phases can spread over the substrate B. In that case there is $\Delta\mu_{2D}<0$, that means such solid or liquid 2D phases exist at undersaturation up to $\Delta\mu=0$ (see (16]). Notice that the Stranski Krastanov growth mode has to be treated in such a context [17].

Kaishew deduced from (6) (7) that every substrate favours kinetically the formation of 3D phases (solid/solid, liquid/solid) since the activation free energy of heterogeneous nucleation is in any case smaller than the activation energy for homogeneous nucleation.

$$\Delta F^*_{hetero}=\Delta F^*_{\text{homo}}\left(1-\beta_{AB}/2\gamma_A\right); \qquad 0\leq\beta_{AB}<2\gamma_A \qquad \textbf{(8)}$$

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[4] When one wants to go to this very limiting case, the surface free energy $\gamma_A(H/a)$ and the adhesion energy $\beta_{AB}(H/a)$ of the thin film A of on a thick substrate B have to be described as a function of the number of monolayers H/a. See the tentative [3] and applications in [15]

This was the first time it was understood that every surface has some catalytic effect with respect to 3D nucleation: $\Delta F^*_{hetero}/\Delta F^*_{homo}<1$. Furthermore one can predict for the crystal A that it is able to make the choice of its AB interface in order to minimize (8) or select AB so that $\beta_{AB}/2\gamma_A \to 1$ provided $\Delta\mu>0$.

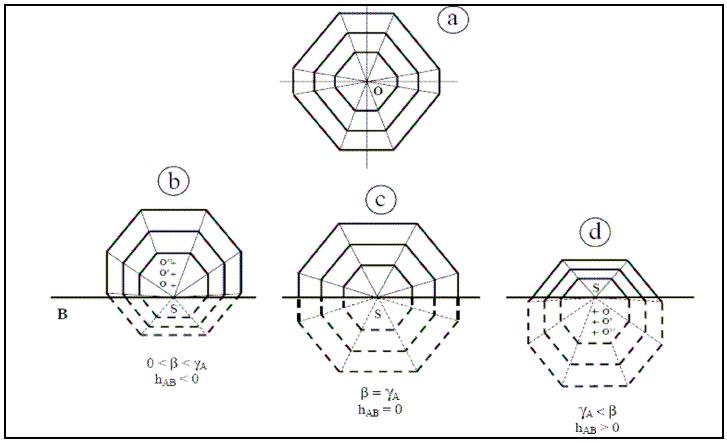

Fig. 1: Equilibrium shapes of free (a) and deposited (b-d) crystals. O are the Wulff points, S the self similarity centre

For a given adhesion ratio $\beta_{AB}/2\gamma_A$ notice that different crystal sizes are self similar. This is quite clear in Fig 1a for the free standing case $\beta_{AB}=0$ where the unique Wulff's point O is a pole of similarity. If $\beta_{AB}>0$, for each crystal size (Fig. 1b and 1d) there are different Wulff points but they do not coalesce with the unique similarity pole S, excepted when $\beta_{AB}=\gamma_A$ (Fig. 1c) for which the Wulff point, located at the interface is common to all the crystal sizes and again becomes the similarity pole S. We underlined this similarity property since we will show in the next section that it is directly connected to the hypothesis of amorphous substrate B or stress free systems.

3. Stressed epitaxial systems

Kaishew's theorem considered the substrate B as amorphous or, if crystalline, it has to be exactly isomorphous with the deposit A (strict

identity and continuity of both lattices)[5]. In both cases the system is in fact not stress free due to surface stress s, an intrinsic surface property (See [3,4]). When a finite size solid phase as a deposit A is formed, it accumulates bulk stress σ and strain ε. For an isotropic solid of cubic shape of side length l, there is $\sigma = -4s/l$ and $\varepsilon = -4\frac{1-2\nu}{E}\left(\frac{s}{l}\right)$, where ν is the Poisson ratio and E the Young' modulus (see [18] p 130 App.A).[6] Notice that such a crystal A is no more isomorphous with its substrate B. Due to its finite size, its crystallographic parameter $a_0 = b_0$ change to $a = a_0(1+\varepsilon)$ so that there is now at the AB interface a misfit $m = (b_0 - a_0(1+\varepsilon))/b_0 = -\varepsilon$ of both lattices. Since s scales $s/E \approx 10^{-9}$ cm, a micron sized crystal A has a very small finite misfit $m \approx 10^{-5}$ compared to the epitaxial misfit, defined for infinite crystals by $m_0 = (b_0 - a_0)/b_0$, accounting usually around $|m_0| \approx 10^{-2}$. In the following we will only consider this latter epitaxial misfit and thus neglect surface stress effects and work when surface areas are changed.

We have to implement now the thermodynamic process ΔF written in 2. One wants to realize a coherent epitaxy of A on B as illustrated in Fig.2

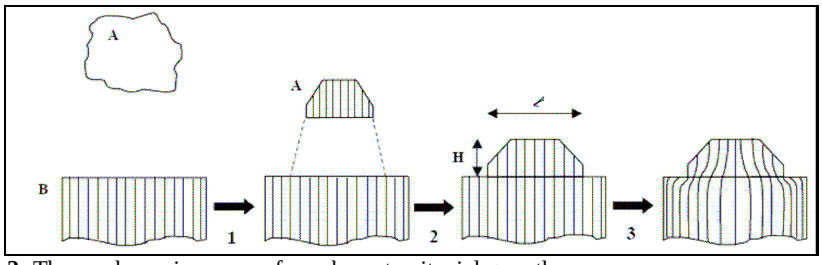

Fig 2: Thermodynamic process for coherent epitaxial growth

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[5] This strict isomorphism does not mean that there must be $\beta_{AB} = 2\gamma_A = 2\gamma_B$

[6] This is the equivalent of Laplace'law for a liquid droplet of radius $r = l/2$ the bulk overpressure of which is $P = -\sigma = 2\gamma_l/r$, γ_l being the surface free energy of the liquid.

Before adhesion of A on B, A needs to be homogeneously deformed to bring its parameter a_0 to the value of b_0 in the interface AB what needs an amount of elastic energy $V'E_0 m_0^2$ for the 2D epitaxial adaptation (E_0 is a combination of elastic constants of the crystals). Crystal A from its free surfaces will relax that means reduce its bulk elastic energy. If coherency is maintained when A relaxes it drags the substrate B increasing elastic energy in it. Both effects can be described by a factor $0<R<1$ reducing the homogeneous energy to $V'E_0 m_0^2 R$ when mechanical equilibrium is reached. The relaxation factor R depends on the shape of the crystal A (and therefore on S_i and S_{AB}) as well as on the elastic constants of the crystal and its underlying substrate so that it can be written $R=R_A+R_B$. This supplementary term has to be introduced in ΔF and $d\Delta F$ in II.

However let us first precise the R factor which has to be calculated for each shape what needs the knowledge of ε_{ij} and σ_{ij} in the interface Z=0 after relaxation. This can be done explicitly only in some simple cases as e.g a rectangular 2D box of height/length ratio $r=h/l$ and relative elastic rigidities K. In terms of R_A and R_B as a function of r for K=1 the result is given in Fig 3c. For more complex polyhedrons as truncated 3D pyramids, only numerical methods are tractable (finite element calculus) . In Fig 3 there are the results of a quadratic based and truncated pyramid (angle θ=45 ° with K=1) taken from [19]. These energy relaxation factors R_A and R_B for both polyhedrons have similar trends. However, full pyramids have the same relaxation factor $R(r\geq 0.5)$=0.45 whatever their size that means the same elastic energy density.

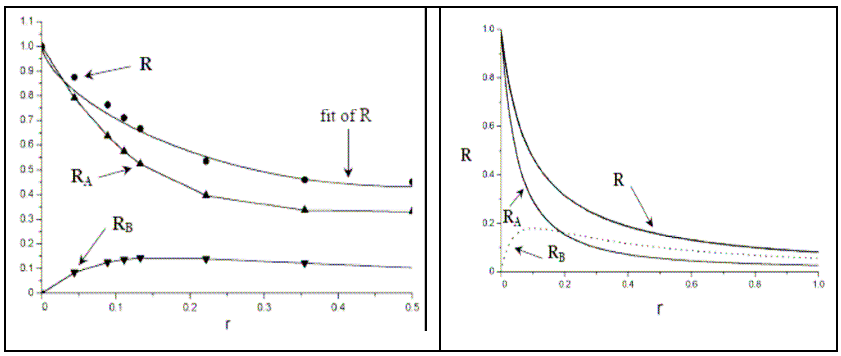

Fig 3: Relaxation factors $R=R_A+R_B$ calculated for a truncated pyramid (left) and a box-shaped crystal (right)

Let us give a road how to find the equilibrium shape in the most simple case of the square based box shaped crystal of volume $V=hl^2$:

$\Delta G=-\frac{\Delta\mu}{2v_c}hl^2+4\gamma_A' hl+(2\gamma_A-\beta_{AB})l^2+E_0m^2hl^2R(h,l)$. The first order differential at constant volume $dV=l^2dh+2hl\,dl=0$ is

$$d\Delta G\big|_V=\left[\frac{\partial\Delta G}{\partial h}\Big|_l-\frac{l}{2h}\frac{\partial\Delta G}{\partial l}\Big|_h\right]dh=\left[E_0m^2\left(hl^2\frac{\partial R}{\partial h}\Big|_l-\frac{1}{2}l^3\frac{\partial R}{\partial l}\Big|_h\right)+(2\gamma_A-\beta_{AB})\frac{l^2}{h}+2\gamma_A' l\right]dh$$

For $d\Delta G=0$, $dh\neq0$, the equilibrium shape fulfils the condition $E_0m^2\left(\frac{\partial R}{\partial h}\Big|_l h_{eq}-\frac{1}{2}\frac{\partial R}{\partial l}\Big|_h\right)-\frac{2\gamma_A-\beta_{AB}}{h_{eq}}+\frac{2\gamma_A'}{l_{eq}}=0$. Calling $r=h/l$, so that $\frac{\partial R}{\partial l}\Big|_h=-\frac{h}{l^2}\frac{dR}{dr}$ and $\frac{\partial R}{\partial h}\Big|_l=-\frac{1}{l}\frac{dR}{dr}$ and calling the aspect ratio in absence of misfit $r_o=h_o/l_o=(2\gamma_A-\beta_{AB})/2\gamma_A'$, the equilibrium condition reads:

$$\begin{cases} h_{eq}=-\dfrac{4\gamma_A'}{3E_om^2}(1-r_o/r)\left[\dfrac{dR}{dr}\right]^{-1} \\ l_{eq}=h_{eq}/r \end{cases} \qquad \textbf{(9)}$$

This is the new Wulff-Kaishev theorem in the form of a parametric system in $r>r_o$. From the elastic data of Fig 3, one computes dR/dr for $K=1$. For a great variety of pure materials one has $\gamma_A'/E_A(1-\nu_A)\approx10^{-9}cm$, taking for the zero misfit case $m=0$, $r_o=0.1$ a very flat crystal, one has

the half self-similar equilibrium shape given in Fig 4a from [20], as well as the non self similar half equilibrium shape for $m \neq 0$

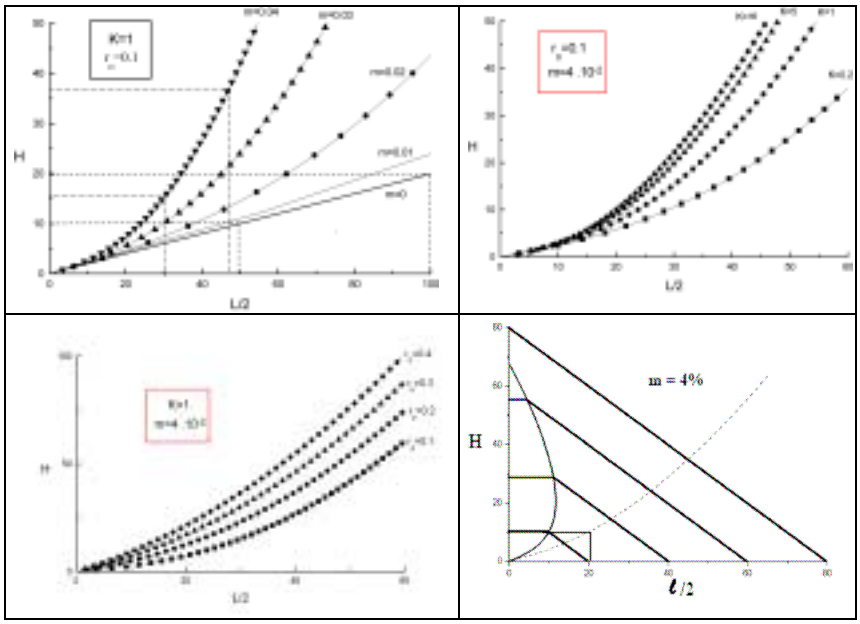

Fig 4: Half equilibrium shapes variation of a box shaped crystal versus misfit (a), wetting factor (b), and relative rigidity (c). The last figure illustrates the equilibrium shape evolution of a pyramid shaped crystal versus its volume. The pyramid changes from truncated to full one.)(For more details see the text)

The equilibrium shape becomes, at constant volume, thus thicker the misfit is greater whatever its sign. Fig. 4b shows for $|m|=0.04$, $K=1$ the effect of the shape ratio r_o, while in Fig 4c is shown the effect of the relative rigidity $K=E_A/E_B$ for r_o =0.1 and $|m|=0.04$ .It results a valuable rule easy to remember: "*wetting (adhesion) flattens the equilibrium shape while epitaxial strain acts against* ". Building more complex equilibrium shapes in presence of epitaxial misfit needs some more trigonometry but the principles are the same. See e.g. [19] for the truncated square based pyramid case whose relaxation coefficient we gave in Fig. 3 at the right for $K=1$ and $\theta=\pi/4$.

The equilibrium shape half profiles are given in Fig. 4 below at the right. For $|m|=0.04$ we draw the trajectory of the edge of the basal face and the pyramid face. Here at some critical size, at a given misfit, the basal face shrinks and the pyramid becomes a full one.

A general remark: We considered only polyhedral crystal shapes, that means only F-faces and in terms of γ-plots, by considering at T=0K, only their inward cusps. Epitaxial strain can only modify crystal faces belonging to these singular γ_A values. No new inwards cusps can be created by this way, what means no new singular faces (F faces) can be created by epitaxial strain. Only surface stress can do this, when surface strain appears by some surface reconstruction. Such considerations have been very scarcely explored theoretically as well experimentally (see [19] p 248-251). The so-called huts have probably such an origin.

4. Plastic relaxation and strained equilibrium shapes

By increasing its size, a coherent epitaxial crystal increases its elastic energy $E_o m^2 V R(r)$ in spite of its elastic relaxation. At some critical size, plastic defects, mostly interfacial dislocations introduce spontaneously. For quadratic based crystals a orthogonal pair of dislocations may appear simultaneously for thermodynamic reasons [7].

These plastic releases are abrupt, reduce the misfit in a discrete way, shorthanded [21] as $m_N \approx m_o - N\left|\vec{b}\right| \Big/ \sqrt{S_{AB}}\Big|_N$ for the N pairs, $\vec{b}$ is the Burger vectors component in S_{AB}. Comparing the self energies of the $2N$ interfacial dislocations accommodating the misfit $m_o - m_N$ with the relaxed elastic energy at misfit m_N one calculates [19] p 236 the critical heights at each entrance N. In Fig 5 a and b we illustrate for the box

[7] Each dislocation enters laterally in the interface for these 3D crystals, but for kinetical reasons, at some bit greater size than thermodynamic equilibrium requires. They enter not necessary simultaneously what shows the curious effect of a virtual small rotation of the crystal at the first entrance, due to Poisson ratio and a back rotation when the second dislocation of the pair enters as was explained by Mathews [21] after the observations of Vincent [22].

shape and the truncated pyramid how the crystal retrogrades its height and facet size by successive saccades at each dislocation entrance.

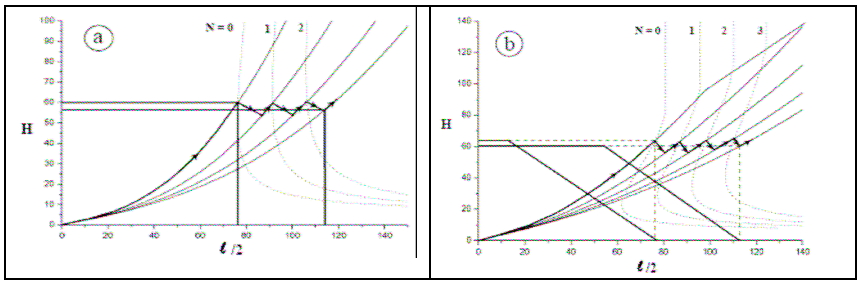

Fig 5: Effect of dislocation entrance on the ES of box shaped crystal (a) and pyramid shaped crystals (b)(For more details see the text)

One imagines an observator scrutizing a truncated growing pyramid (not depicted in Fig 5b) becoming higher, loosing continuously its summital face. By further growing he has the surprise to see the reappearance of the facet suddenly, becoming greater and flatter by saccade ! He does not see the dislocations. Such shape ratio changes have been really observed by several authors on semiconductor epitaxy in situ by electron microscopy following the shape change at each observed dislocation entrance [23]. We referred more completely about such facts in [19] p 248-251.

5. Strain-stress fields outside epitaxial contacts

When relaxing a coherent epitaxial crystal A transmitting to its substrate B part of its strain and stress fields to its volume and surface[8] . In Fig 6. we give the tangential strain components at the interface Z=0 of a box-shaped ribbon $r=h/l$ along the contact $-1<X=2x/l<1$. In A and B they are necessarly complementary when their proper reference states are used: $\varepsilon_{xx}^{A}(X,0)+\varepsilon_{xx}^{B}(X,0)=m_o$. Outside this contact area $X>1$, $X<-1$ the substrate at Z=0 suffers also strain but a tangential dilatation when the inside is contracted and vice versa.

[8] This is true for every type of contact solid or liquid on solid but with very less extent e.g. glissile epitaxy or on amorphous substrate.

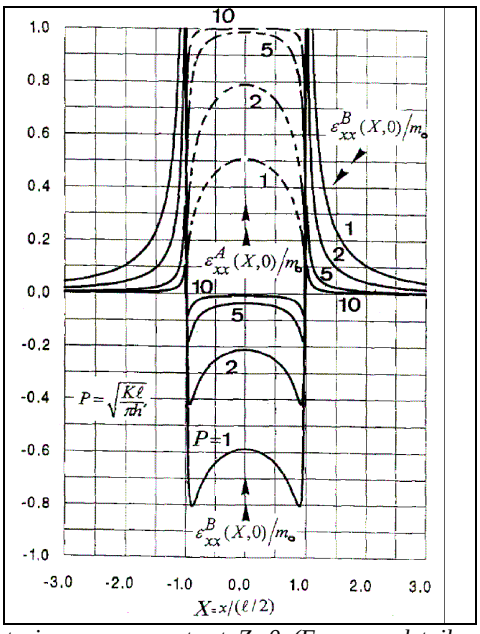

Fig 6: *Substrate strain xx components at Z=0. (For more details see the text)*

With such kind of "antenna" the epitaxial dot A is able to communicate elastically with other strain-stress generators located in the bulk or the surface of B. Such generators[9] may be other dots, foreign atoms or clusters, point defects and their clusters in the bulk or the surface of B or simply surface steps etc… Notice that the well-known surface defect decoration technique of Basset and Bethge' school finds herein its rationality [24]: opposite sign strain bearers attract each other, same sign field bearers repulse each other.

In the 70th, in a series of papers we summarized in [25,26,16], experiments showing that metal 3D clusters of Au, Al of ≈ 2 nm diameter give glissile epitaxies on the (100) cleavage of alkali halides crystals. They start to glide and rotate by maintaining the (111) (100) contact at moderate 80-150°C temperature and the system remains conservative that means the collection does not change its size histogram.

[9] This is true for isotropic elasticity but needs more care for general elasticity even for cubic crystals, except for their high symmetry contact faces.

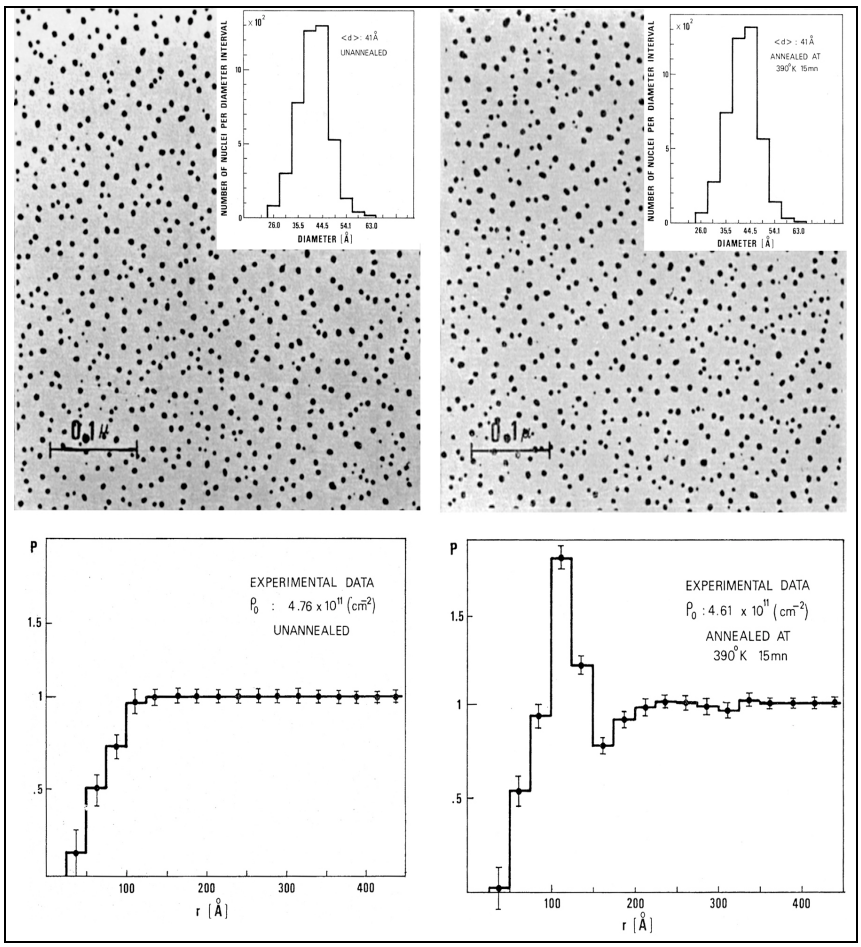

Fig 7: Glissile epitaxy Au(111)/KCl(001) from [27]

In Fig 7, at the left, one sees the as deposited crystals at room temperature (Au/KCl) and size histogram with below the corresponding radial distance distribution $P=g(r)dr$. In Fig 7c the same sample but after several minutes of annealing at 120 °C and size histogram gives below its $g(r)dr$ showing that (i) the crystals moved, (ii) that the crystals interact. From the quantitative analysis of the $g(r)dr$ one could (iii) deduce that they interact elastically in a repulsive manner $\approx r^{-4}$. This $g(r)dr$ at the right below is the signature of an embryonic "self-organisation " similar to

that one obtains for a dilute 2D gas. May be that higher cluster densities will have a better tendency to organise as illustrated in Fig 8 for Pd(100) clusters on (100) MgO around 550° C taken from [28].

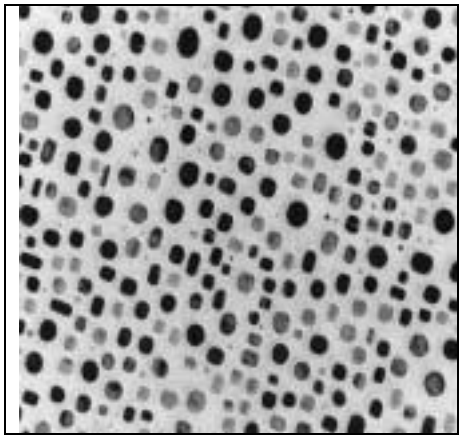

Fig 8: Pd (100) on MgO (100) (Courtesy of C. R. Henry)

Here surface diffusion, elasticity, Ostwald ripening, coalescence have been at work. There is some illusion of periodic self-organisation, the dream of many integrated circuit technicians. May be that a choice of anisotropic partners A/B with some in-plane, positive-negative alternation of strain lobes as described by [29] will bring better ordering but attainment of periodicity is doubtful. Let us mention that recently [30] similar results as ours have been obtained with in-situ Electron Microscopy observations on 3D Ag dots on hydrogenised Si(111) wafers. The interpretation is less quantitative but computer simulation of structure and energy of glissile interface is convincing.

Recent kinetic Monte Carlo simulations [31] allowed modelling the growth of strained dots with the ingredients of semi-conductors systems. The strain field creates some 2D ordering and is said to narrow the size distribution of the collection of dots. We think latter point is not quite understood. One knows usual Ostwald ripening (without strain) leads to eliminate the smallest clusters in the neighbourhood of bigger ones due to exchange of adatoms (Wulff-Kaishev theorem is responsible of that (see (6,7)). When strain is present the overlapping of the strain fields regulates furthermore the shape ratio of the neighbouring clusters and the material exchange by adatoms. What remains true is that the bigger clusters eat the

smaller ones in the neighbourhood[10] what already was said by Curie, so at the real end there remains only one crystal. Let us furthermore remember that at some critical size the crystals plastically relax and go up to near zero strain, behaving then according usual Ostwald ripening.

6. Towards 3D organisation

Usefull 2D organisation of dots in semiconductor systems is realised currently by photographic processus to lower limits of several $10^{-1}\ \mu m$ periods. More sophisticated is [32] the idea and realisation of strain mapping on the surface of thin wafers brought together as Si(100) in close atomic planar contact but e.g. with some azimuthal small angular misorientation. The interface bears two orthogonal arrays of dislocations. The in-plane strain and stress field of this array intersect the surface of so welded wafers similar to a Moiré pattern with its periodic minima and maxima. It is clear that at the location of the minima of this strain field one has the opportunity to deposit epitaxially a material preferentially near these loci where one has minimal misfit. Nice 2D periodic arrays of dots have been obtained. There are some limitations of the metric of the coincidence lattice. Great inter dot spacing are more easy to obtain than smaller ones.

Some authors in the 90th have observed that when coherent islands A are covered with materials B of the substrate that when fully buried in B the new planar surface has some "memory" of the location of the underlying dots. Strain fields have been calculated at the surface of an isotropic elastic materials when the generator is located in the bulk [33] so that Tersoff [34] proposed to study and fabricate 3D superlattices of 3D strained dots with (Si,Ge) on Si or InAs (or InGaAs) on GaAs. One has to start with strained dots A far smaller than their critical size to avoid entrance of dislocations, buried by the material B of the substrate and obtaining again a flat surface but bearing an attenuated strain field able to receive new dots A [33]. Tersoff simulated many such depositions and observed that the island size and spacing become progressively more uniform. Experimental confirmation could be obtained on the system $Si_{¼}Ge_{¾}$ /Si(001) with 20 consecutive layers (Si spacer $10\ nm$, alloy

[10] However, this can be wrong if two different shapes or orientations can coexist on the surface. Indeed, in this case, two crystals of different sizes and different shapes may have the same chemical potential.

2.5 *nm*). Regularity increases with number of layers as well in shape, size and pseudoperiodicity, latter being however not of better quality than that one we depicted in Fig. 8.

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