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ON CONTINUUM MODELLING OF SURFACE NANOPATTERN EVOLUTION

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1. INTRODUCTION

Surface roughness has a huge impact on many important phenomena. Typical examples of spatiotemporal pattern formation in systems driven away from equilibrium can be found in physical, chemical and biological processes such as in hydrodynamic systems in pure fluids and mixtures, in patterns of solidification fronts, in optics, in chemical reactions and in excitable biological media [2]. While on micro- and macro scales one can control the processes by special devices, on nano scales such instruments are absent or their use is extremely expensive. Therefore, the investigation of self-organization and self-assembly provide promising mode to understand basic physical principles and mechanisms. The understanding of these processes can allow us to extend the use of such technique to a large variety of fabrication processes, to create new electronic devices, sensors and tailored surfaces; moreover, to controllably modify chemico-physical properties of the surface by tailoring the nanoscale morphology during patterning and to optimize certain film properties like roughness and coarsening.

In many industrial applications a thin film of a solid material needs to be deposited on a solid semiconductor substrate. This deposition can be made by different methods, e.g., by ion beam sputtering or Chemical Vapour Deposition (CVD), and during the growth process atoms of the film stick to the atoms of the substrate at its surface. Usually, the growing film does not remain planar during its growth and various kinds of surface structures are developed. The types of these structures depend on physical characteristics of the materials as well as on the growth conditions.

The main objective is to introduce deterministic equations that describe physical phenomena and their solutions are most likely received from the initial condition and will remain valid even after a long time.

Surfaces can be smooth but the same surface can also be rough. Surfaces with “ideal” topography, e.g., prepared by fracture or by some growth process, have

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been studied intensively for many years [2-6, 8]. An important question is how we can describe the morphology and how to study surface and interface dynamics.

2. MODELING

In the mathematical approach, it is important to incorporate the uncertainty of the parameters into the model. The main sources of uncertainties are difficult to predict. These include the elastic interaction at atomic level, surface state changes and others. The irregular surfaces are characterized by partial differential equations together with free boundary conditions. To find analytical solution to these partial differential equations is usually impossible, the applied numerical algorithms are generally unstable, and therefore variation methods have to be used. With this approach, the singular geometries can also be treated.

The theoretical base is the system of partial differential equations. The deterministic equations of motion are usually non-linear differential equations. They are sometimes supplemented by stochastic members, which represent temperature or instrumental noises. In carefully designed experiments on macro scale stochastic forces are negligible. Some aspects of self-assembly of quantum dots in thin solid films are considered. Nonlinear evolution equations describing the dynamics of the film instability that results in various surface nanostructures are analyzed in the literature [9-16]. Pattern formation is analyzed by means of amplitude equations.

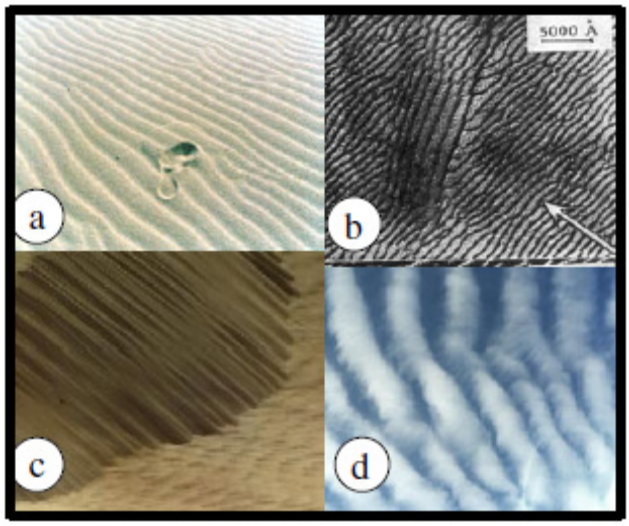

Figure 1. The same experiment as in [18] compared with sand ripples observed in the desert [23]. (a) Sand ripples on a dune in an Australian desert. (b) Glass surface after 6 h bombardment, $\theta = 45\circ$. The arrow indicates the projection on the surface of the ion beam. The effect is similar to that reported in (c) for the sand dune. (c) Sand ripples on a dune in a desert (Algeria). The ripples on the dune have different

orientation with respect to the ripples in the open desert. (d) The clouds are the tops of the ripples between the dry, cool air above and the moist, warm air below.

Reports on the production of submicron and nanometric patterns on the surfaces of solid targets eroded by ion irradiation are dated back to the 1960s. In 1956 Navez *et al* [19] observed the phenomenon, that bombarding a glass surface with an ion beam of air, the bombardment produced a new morphology depending mainly on the incidence angle θ of the ion beam. The obtained surface is covered by wavelike structures (ripples) separated by distances ranging from 30 to 120 nm. The authors tried to find analogies with macroscopic phenomena such as the ripple structures formed by wind over a sand bed. The observed formations in sand dunes and in clouds are very similar to the features observed on the glass modified by ion bombardment [22] when air and sand come into contact, as they can be considered as two immiscible fluids. Air and sand can be moving at very different speeds. The boundary between them can develop complex wavelike structures and ripples. The morphologies of sand dunes are qualitatively similar to that obtained by sandblasting.

One of the typical features of quantum dots is that they formed spontaneously due to the instability of a thin solid film deposited on a solid substrate. Therefore, one can talk about self-assembly of quantum dots. The self-assembled quantum dots can have various shapes: regular, as faceted pyramids; irregular, as small crystals with many facets in various orientations; rounded, as cones [12].

When an array of quantum dots formed on the surface of a solid film is kept at a fixed temperature, the dots can either exhibit coarsening or not. During coarsening the larger dots grow at the expense of the smaller ones so that the average dot size increases in time. In the absence of coarsening, the dot size distribution does not essentially evolve at all. The mechanisms that govern the shape of quantum dots, the dynamics of their formation and the evolution of the quantum dot arrays are expressed in several models.

The principal mechanisms that govern the formation, morphology and evolution of quantum dots are elastic stress, anisotropic surface energy and surface diffusion. Since the 1960s surface pattern formations have been found on the variety of materials. The periodicity of the ripples can be tuned by bombarding the surface with varying energy of ions (typically in the range of 0.1 to 100 keV). Depending on the angle of incidence of the ion beam the surface ripples can be oriented parallel or perpendicular or hexagonally ordered.

Surface-energy anisotropy is responsible for the equilibrium shape of a given material with a fixed volume which minimizes the total energy of its surface. If the surface energy of the material is isotropic (that is a constant), the equilibrium shape must minimize the total surface area. When the volume is fixed this minimization is provided by a spherical shape. When the surface energy is anisotropic and depends

on the surface orientation, a shape that minimizes the total surface energy, under the constraint of a fixed volume, is no longer spherical. It is given by a solution of a corresponding variational problem that leads to a nonlinear partial differential equation of the second order for the surface shape.

During the mechanism of instability of a thin solid film deposited on a solid substrate, the substrate can prescribe the film to grow in a specific orientation that would have been forbidden in the absence of the substrate. When the film becomes thick enough and does not “feel" the substrate any more it will undergo faceting instability and decompose into a system of faceted islands.

Theoretical predictions for surface structures are derived by partial differential equations involving the derivatives of a time dependent height function $h(x,y,t)$ of the surface, describing film growth at a mesoscopic level. Numerous conservative continuum equations have subsequently been proposed [13], since in many practical situations the dominant surface relaxation mechanism is surface diffusion, with vacancy formation and particle desorption being quite negligible. Usually such models admit main contributions related to both local dynamics, chemical reactions type of birth and deaths processes, and mass transport [15]. In testing the validity of the theory it is important to identify the right terms of the evolution equation.

(i) The Edwards–Wilkinson (EW) model plays an important role in the study of non-equilibrium surface growth due to the simplicity of its growth process. A lattice model was introduced for the study of fluctuations in a surface, growing by random deposition of particles with immediate relaxation to nearest-neighbour sites. Based on the lattice model, Edwards and Wilkinson derived an equation which is purported to describe the surface fluctuations during growth. The EW equation is written as

$$h_t(x,t) = \nu \nabla^2 h + \eta(x,t), \qquad (1)$$

where ν is the surface tension, and η is the stochastic contribution to the surface fluctuations.

It is important to note that the linear evolution equation (1) is mathematically ill-posed, unbounded growth of short wavelength models appear.

(ii) The Kardar, Parisi and Zhang (KPZ) model [2], is a very well-known example of the growth process, suggested a continuum equation which does not conserve particle number, and is therefore applicable to cases where desorption and/or vacancy formation, but not surface diffusion, are the dominant surface relaxation mechanisms.

It was introduced in the context of studying the motion of growing interfaces for connections between polymers and lattice gases in [14]. Experimental observations caught the imagination are published for

many applications. For example, physical phenomena modelled by the KPZ class include turbulent liquid crystals, crystal growth on a thin film, facet boundaries, bacteria colony growth, paper wetting, crack formation, and burning fronts [2].
The time derivative of the height function depends on three factors: smoothing (the Laplacian), rotationally invariant, slope dependent, growth speed (the square of the gradient), noise (spacetime white noise)

$$h_t(x,t) = \nu \nabla^2 h + \frac{\lambda}{2}(\nabla h)^2 + \eta(x,t) \tag{2}$$

where η is white Gaussian noise and ν and λ are non-zero parameters which can often be (heuristically) computed for a particular growth model directly from the microscopic dynamics.

(iii) One widespread example of the "Molecular Beam Epitaxy" (MBE) model, where material is slowly evaporated onto the surface at sufficiently high temperature. This deposition produces a film which bears an epitaxial relation to the substrate. The growth process of surface formations is regularized by surface diffusion. The evolution equation for the shape of the film surface can be written

$$h_t(x,t) = -K \nabla^4 h + \lambda_2 \nabla^2 (\nabla h)^2 + \eta(x,t), \tag{3}$$

where K and λ_2 are parameters. The smoothening term $-K\nabla^4 h$ expresses the surface diffusion. This expresses the evolution of a thin epitaxial film in the case when the film instability is caused by the epitaxial stress, the film surface energy is isotropic, and the film is thin enough so that wetting interactions between the film and the substrate are important.

(iv) The appearance of step instabilities can be described by the evolution equations. In the growth process two different types of instability may appear [21]. On of them is the step bunching when the density of steps does not keep constant. The steps prefer to gather in bunches separated by large terraces. Step bunching occurs while steps are straight, i.e., the dynamics can be described by 1+1 dimensional equations. In the presence of large desorption it can be modelled by

$$h_t(x,t) = -\nu h_{xx} + \gamma h_{xxx} - K h_{xxxx} + \lambda [h_x]^2, \tag{4}$$

where γ and ν are parameters and $h = h(x,t)$ is the rescaled step shape in stepwise direction x. The term $-\nu h_{xx}$ is responsible for the instability, the second term expresses the surface energy and surface

diffusion, the third nonlinear term is proportional of the coarsening dynamics at long time [24].

(v) The second type of instability, the step meandering when steps do not stay straight and start wandering. The dynamics of meandering depends on the asymmetry in the attachment. In the presence of strong evaporation the Kuramoto-Sivashinsky (KS) equation is used

$$h_t(x,t) = -\nu\, h_{xx} - K\, h_{xxxx} + \lambda [h_x]^2 , \tag{5}$$

which one is obtained from (4) with $\gamma = 0$. It is the typical equation of the spatio-temporal chaos. KS equation is derived for both electrochemical deposition (ECD) and chemical vapour deposition CVD.

(vi) In case of vanishing desorption and weak symmetry, the growth process and the rise of coarsening pattern are modelled by the conserved Kuramoto-Sivashinsky (CKS) equation.

$$h_t(x,t) = -\nu\, h_{xx} - K\, h_{xxxx} + \lambda_2 [h_x]^2{}_{xx} . \tag{6}$$

The term $-\nu\, h_{xx}$ is responsible for the instability, the nonlinear term $-\lambda_2 \left| h_x^2 \right|_{xx}$ is proportional to the flux. Experiments suggest that CKS describes the surface dynamics for MBE.

(vii) Anisotropic coarsening for the height fluctuations $h = h(x, y, t)$ is described when the height deviates from the mean slope

$$h_t(x,t) = -h_{xxxx} - A h_{xxx} - \left| h + h_{yy} + (h_y)^2 + B h_x + C h_{xx} \right|_{xx} , \tag{7}$$

where A, B, C are parameters. The meandering instability is described by the term $-h_{yy}$, the relaxation processes due to elastic step interactions are taken into account with terms having an even number of x derivatives, the step stiffness is incorporated in term $-h_{yyyy}$; the term proportional to A is related to the dispersive nature of the step flow, the nonlinear term $-\left(h_y^2\right)_{yy}$ is responsible for the coarsening.

The boundary conditions indicate the stress and the displacement continuity at the film-substrate interface. The governing equation is considerably simplified if the small-slope approximation is used, assuming that the slopes of the emerging surface structures are small.

Numerical solutions to equations (1)-(7) in 1+1 or 1+2 dimensions by means of a pseudospectral method can be obtained with periodic boundary conditions. One can observe the formation of hexagonal arrays of dots or pits in the parameter regions predicted by the weakly nonlinear analysis. It is interesting that, similar to the 1+1 case, the formation of two types of dots is possible: “cone”-like and “cap”-like. With the increase of the supercriticality “cones” transform into “caps”. It is known that hexagonal patterns can become unstable with respect to patterns with other symmetries

Results of the numerical simulations to equations (1)-(5) show the transition from hexagonal arrays of dots or pits to stripe patterns (“wires”) with the increase of the supercriticality. Transition from dots to wires in epitaxially strained films has been observed in experiments [23].

The numerical solutions also show that quasiperiodic dodecagonal arrangement of dots can be formed. However, this dodecagonal structure occurs only at the beginning of pattern formation; later in time it either gets replaced by a hexagonal structure, or grows further and ultimately blows up.

3. SURFACE ROUGHNESS

A common feature of most non-equilibrium interfaces is that their roughening follows simple scaling laws [5]. This phenomenon is also observed experimentally. Here we define the mean height function $\bar{h}(t)$ at the time t for $t \in [0,T]$ by

$$\bar{h}(t) = \frac{1}{|\Omega|} \int_{\Omega} h \, dx$$

where $|\Omega|$ is the area of $\Omega = [0,L]^2$. All rough surfaces exhibit perpendicular fluctuations which can be characterized by the surface roughness

$$w(t) = \sqrt{\frac{1}{|\Omega|} \int_{\Omega} |h(x,y,t) - \bar{h}(t)|^2 \, dx}$$

for $t \in [0,T]$.

In 1985, Family and Vicsek [7] introduced the notion of "dynamic scaling" in order to incorporate both temporal and spatial scaling behaviors.19 Within this context, the evolution of the (saturated) rms width with deposition time t is characterized by a "growth" exponent β, according to σ is proportional to t^{β}. It is assumed here that the film thickness is directly proportional to the amount of material deposited and that the deposition rate is constant. The spatial and temporal scaling behaviours of films grown under non-equilibrium conditions can then be combined into the dynamic scaling form [1, 16]

$$w(L,t) = L^{\alpha}\, F\left(t / L^{\alpha/\beta}\right),$$

where $0 < \alpha < 1$ is referred to as the "roughness" exponent for the interface h and α/β is the dynamic exponent which describes the scaling of the relaxation time with system size L. The scaling function f has special properties, which indicates that $w(L)$ tends to a constant value L^{α} when $t / L^{\alpha/\beta} \to \infty$ and $w(L)$ is proportional to t^{β} when $t / L^{\alpha/\beta} \to 0$.

For the film growth, described by the KPZ equation, is associated with the exponents $\alpha = 0.385$ and $\beta = 0.240$, and for evolution described by (3) one gets $\alpha = \beta = 0$ [16].

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