PRAMANA
— journal of
physics

Vol. 58, No. 2
February 2002
pp. 399–408

Growth of rough epitaxial surfaces

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Abstract. We present here a set of coupled continuum equations to describe atomic deposition. We take into account evaporation due to thermal and mechanical disturbances as well as subsequent accretion at favourable grooves.

Keywords. Atomic deposition; roughness; continuum equations.

PACS Nos 71.20; 71.20c

1. Introduction

During the last decade, the physics of surface growth has become a burgeoning area of research, involving separate attempts of the statistical physics and the electronic structure community. In this paper we attempt to unite these viewpoints to provide a more holistic framework within which such growth can be studied.

Several theoretical attempts [1] through discrete and continuum models of kinetic roughening have been made, motivated by experiments, which are of paramount technological and industrial importance. Experimental techniques like molecular beam epitaxy (MBE) and chemical vapor deposition have made possible the development of a number of useful devices. Most of these need smooth interfaces for good contact. However, roughening is often an inevitable part of surface formation, so that an understanding of the surface morphologies has a crucial part to play in the many vital applications of this field. High temperature MBE growth produces good quality two-dimensional flat multilayers which are investigated using reflection high-energy electron diffraction (RHEED) where the interface roughness oscillates with time. MBE surfaces grown at low temperatures exhibit three-dimensional structures over the interface, enriched with steps and islands.

The division between the communities is illustrated most tellingly by the following: almost all the continuum and discrete models of MBE growth have so far only inserted empirically obtained parameters as inputs for their kinetic processes. On the other hand, attempts to study interface growth via the methods of electronic structure have usually involved computational approaches such as kinetic Monte Carlo, and have stopped short of trying to provide the analytical understanding that macroscopic continuum equations provide of aspects like interface roughness. In our bid to bridge this gap, we study in this work a model system of coupled stochastic continuum equations and use *ab initio*

electronic structure techniques on the surface structures produced by it to at least partially justify the structure of the equations proposed by us.

We shall borrow some of the ideas prevalent in the related field of granular media [2,3]. While most theoretical approaches so far [4] have focused on the response of a driven pile via flowing grains down its surface, alternative approaches to this problem [5–8] have always emphasized the *coupling* between the moving grains and the relatively immobile clusters and its impact on sandpile dynamics.

Our aim is to adopt some of the techniques available in the study of granular sandpiles and suitably adapt them to the related problem of atomic deposition.

2. The statistical model for atomic deposition

Atomic deposition has many features in common with granular deposition. The added feature is atomic binding. In the usual deposition geometry, a randomly fluctuating flux of atoms is incident on a substrate. Atoms deposit on the surface of the substrate and diffuse along it to minimize the energy. A cloud of unbonded atoms envelope this deposit and continuously exchange atoms with it through evaporation and re-deposition.

While non-equilibrium growth has been extensively studied by coarse-grained classical stochastic equations [9], it is not obvious *a priori* that the microscopic energetic constraints relevant to atomic surfaces would automatically be satisfied by largely heuristic classical terms. We therefore have to present electronic energy calculations in support of our model of surface growth.

Among various physical processes which have been taken into account in models of growing interfaces, *surface diffusion* has been considered as the most important process involved. One such model involves the linear fourth-order Mullins–Herring continuum equation [10,11] supported by the discrete model of Wolf and Villain (WV) [12]

$$\partial h(\mathbf{x},t)/\partial t = -\kappa\nabla^4 h(\mathbf{x},t) + \eta(\mathbf{x},t), \tag{1}$$

where $h(\mathbf{x},t)$ is the height of the interface from some mean height $\langle h(\mathbf{x},t)\rangle$ and $\eta(\mathbf{x},t)$ represents Gaussian white noise as usual. This equation yields a large roughness exponent $\alpha = 1.5$ in $d = 1$.

Although there have been a number of non-linear equations which add to this simple linear description [13] of surface growth, there have been rather few attempts so far to look separately at the roles of relatively immobile atoms which are bonded to the surface (forming clusters) and the cloud of mobile atoms above the surface. The latter arise both from the impinging atomic beam and from evaporation caused by atoms knocked out of the surface by thermal or mechanical disturbances. These are described by their local density $\rho(\mathbf{x},t)$. We propose a new class of growth equations with an explicit coupling between the profile of 'bonded' atoms represented by the local height of the surface $h(\mathbf{x},t)$, and 'mobile' atoms on the surface represented by their local density $\rho(\mathbf{x},t)$. Our equations read

$$\begin{aligned} \partial h/\partial t &= -D_h\nabla^4 h - \mathscr{T} + \eta_h(\mathbf{x},t), \\ \partial\rho/\partial t &= -D_\rho\nabla^2\rho + \mathscr{T}. \end{aligned} \tag{2}$$

In an earlier paper [14], transfer term $\mathscr{T}$ was given by

$$\mathscr{T} = (\nu - \rho)|\nabla h|.$$

However, for bonded atoms, as in our present study, since evaporation occurs preferentially for weakly bonded atoms and accretion at points where bonding is maximally favoured, an alternate model could be

$$\mathscr{T} = \nu|\nabla^2 h|(1 - \Theta(\nabla^2 h)) - \rho|\nabla^2 h|\Theta(\nabla^2 h), \tag{3}$$

where $\Theta(x)$ is 1 if $x > 0$ and 0 if $x \leq 0$. We describe in what follows the meaning of the above terms. In items (i) and (ii), we describe those terms which are specific to a single species, whereas in items (iii) and (iv) we describe the coupling terms included in the transfer term $\mathscr{T}$.

(i) The fourth-order term in eq. (2) describes surface diffusion of bonded atoms; this is the usual WV [12] term where $\mathscr{D}_h$ represents a diffusivity. The particle current leading to this term is the gradient of the local chemical potential, which is assumed to be proportional to the local curvature.

(ii) The flowing grains are neither bonded to one another nor to atoms on the surface. The first term in (2) hence describes normal, as opposed to surface diffusion of the mobile atoms, where the corresponding current is the gradient of the density.

(iii) The first term in the transfer term $\mathscr{T}$, eq. (3), describes spontaneous generation of mobile atoms on the surface of *evaporation*. This could be due to 'vibration' caused by, for example, thermal disturbances. We have assumed that it is easier thermally to eject atoms weakly bonded at points of high negative curvature (sharp peaks). ν then is a measure of the substrate temperature.

(iv) The second term in $\mathscr{T}$, eq. (3), represents 'condensation', whereby mobile atoms accumulate and accrete preferentially at deep grooves (high positive curvature).

(v) Finally the last term in (2) is a Gaussian white noise characterized by its width Δ_h

$$\langle \eta_h(\mathbf{x},t)\eta_h(\mathbf{x}',t')\rangle = \Delta_h^2 \delta(\mathbf{x}-\mathbf{x}')\delta(t-t').$$

We assume that growth occurs on a flat substrate; this and the absence of a preferred direction causes us to consider always the absolute values of slope in the above equations. We emphasize that our modeling in the above equations represents the well-known physics of MBE (ref. [12]), via surface diffusion of interfacially bonded atoms, ordinary diffusion of mobile atoms above the interface, and the inter-conversion of one species into the other via evaporation and condensation.

We can visualize the following sequence of processes: first, the mobile atoms diffuse $(\nabla^2\rho)$ in the cloud above the surface. This is followed by the preferential conversion of these atoms into the bonded species at deep grooves (large positive $\rho\nabla^2 h$) on the surface. The term $\nu|\nabla^2 h|$ at mounds, models the effect of evaporation, leading to a dynamical exchange at regions of high slope between bonded and unbonded atoms. However, the action of the $\nabla^4 h$ term is to stabilize the formation of mounds and grooves and so ultimately the overwhelming effect is a roughening of the surface. Figure 1 illustrates the effect of the terms in our model.

We have simulated the above equations in $d = d' + 1$ dimensions, with $d' = 1$ where d' is the substrate dimension, in order to extract the critical roughening exponents α and β. These are defined by the following scaling relations involving the correlation functions $S(k,0)$ and $S(0,\omega)$:

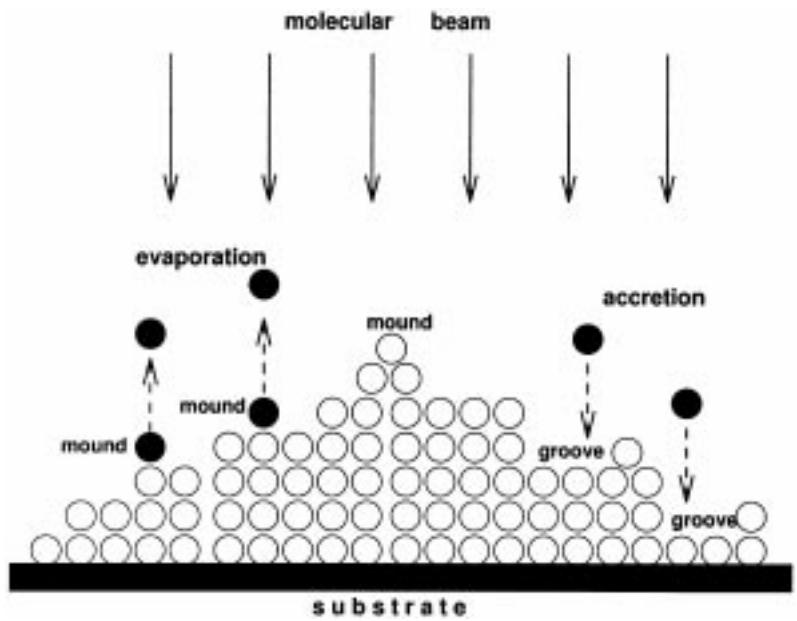

Figure 1. A pictorial depiction of the model.

$$S(k,0) \sim k^{-1-2\alpha},$$
$$S(0,\omega) \sim \omega^{-1-2\beta}.$$

A one-dimensional lattice was used in our simulations, with periodic boundary conditions. Finite size checks were also carried out, in order to eliminate spurious effects arising from this in the determination of our critical exponents.

Figure 2 presents the correlation functions $S(k,0)$ and $S(0,\omega)$ for h and ρ for a simulation of the coupled equations.

Our results are:

(a) $\alpha_h = 1.61 \pm 0.02, \beta_h = 0.39 \pm 0.02.$
(b) $\alpha_\rho = 1.325 \pm 0.025, \beta_\rho = 0.465 \pm 0.01.$

The exponents for h indicate that the dynamical exponent is given by $z_h \sim 4$, consistent with most models for MBE growth, and indicating that the fourth-order term plays a dominant role in the dynamics, as it should. However, the value of α_h is greater, given the error bars, than the pure WV value of 1.5; this suggests that additional roughening is caused by the transfer term $\mathscr{T}$, which is therefore relevant in the renormalization-group sense. The role of the transfer term $\mathscr{T}$ is even more obvious in the critical exponents for ρ, where we get *super-roughening* in the mobile atoms. It is obvious that this can only arise from the transfer term, since without this one would have got diffusive exponents pertaining to the linear equation. The physics of this is as follows: the action of the $\nabla^4 h$ term is to build up mounds and grooves on the bonded interface, as is well-known. These then provide

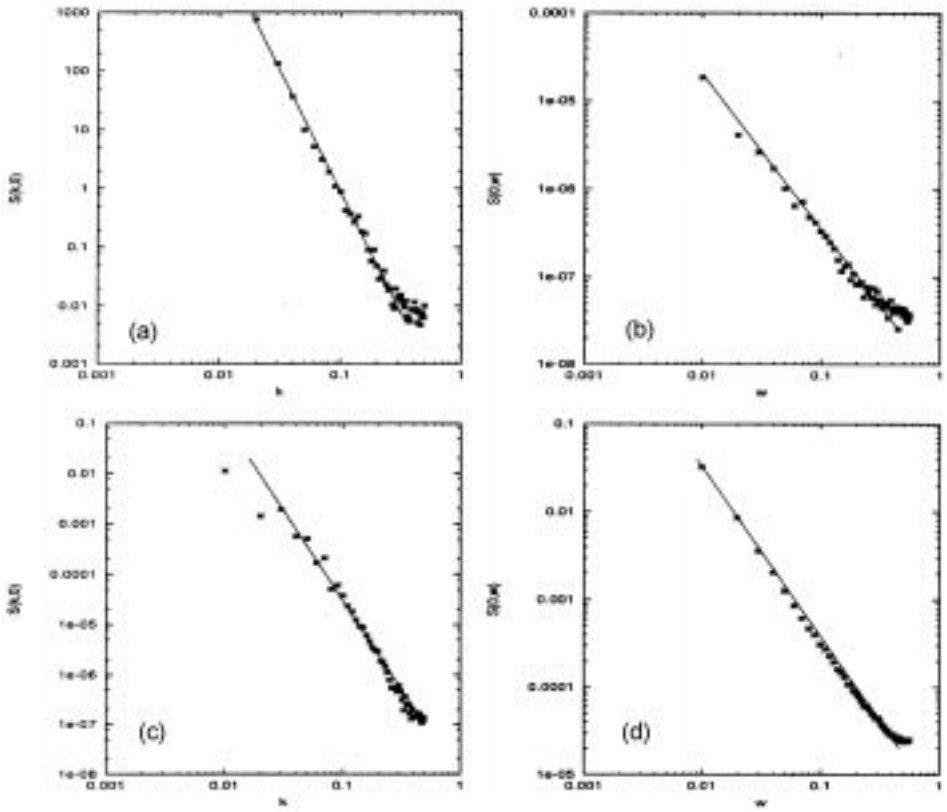

Figure 2. (**a**) $S(k,0)$ for the h–h correlation function. (**b**) $S(0,\omega)$ for the h–h correlation function. (**c**) $S(k,0)$ for the ρ–ρ correlation function. (**d**) $S(0,\omega)$ for the ρ–ρ correlation function.

excellent sources of mobile atoms, because of the action of the $\nu|\nabla^2 h|$ term, in dislodging weakly bonded atoms from the local mounds. This/it is preferential generation of mobile atoms in certain regions of the interface is what causes the excess roughening of the ρ profile, as manifested by the large exponents for α_ρ and β_ρ compared to a simple $\nabla^2\rho$ diffusive growth.

3. Energetic justification of the deposition equations

Before proceeding further, we shall first consider the justification of our coupled equations from energy considerations. We have already mentioned that, as opposed to simple sandpiles, atomic deposition involves atomic binding by the valence electron cloud. It is not *a priori* obvious that the heuristic terms included in our equations are satisfied when binding is included.

We shall take the example of Fe deposited on the (100) surface of a Ag substrate. The face diagonal of body centered cubic iron, the most commonly known ferromagnet,

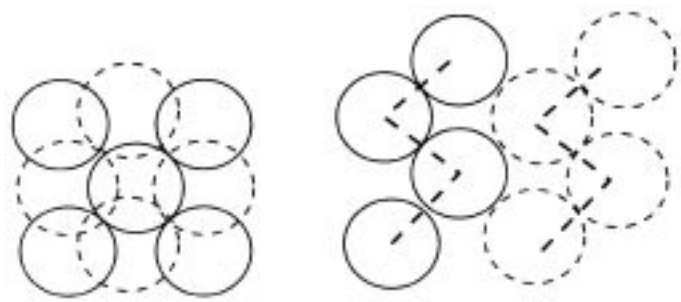

Figure 3. Top and side views of face centered cubic stacking. The lines denote the atoms in the two levels which belong to the same height column.

matches with the lattice constant of face centered cubic silver, a very good non-magnetic electrical conductor. This favors epitaxial deposition of body centered cubic Fe on Ag (100) manifesting interesting magnetic properties.

The first step would be to produce a rough surface profile from the coupled equations. The next step would be to discretize the continuous height variables $h(\mathbf{x},t)$. For the square lattice this discretization is straightforward. For a face centered cubic lattice the heights can be thought of as produced by atoms which are vertically stacked with every alternate layer displaced by half the lattice distance along any one direction. The top and side views of such a stacking are shown in figure 3.

The rough surface on discretization then yields a random arrangement of Fe atoms on the body centered cubic growth on the face centered cubic Ag substrate. We should note that translation symmetry is lost in all three directions. At the substrate-overgrowth interface, translation symmetry does obtain in directions parallel to the 100 surface, but is lost in the direction perpendicular to it. Within the rough surface, however, we do not have translation symmetry in any direction. So the entire calculation must be carried out in real space. Although a coherent potential calculation has been suggested in which we model the rough surface as a binary alloy between the constituent atoms and *empty spheres*, it is doubtful whether the homogeneous randomness which is at the base of the coherent potential approximation is suitable for describing the roughness involved. We shall turn to the recursion method [15]. The method was first introduced for the study of systems without translation symmetry and its advantage lies in the fact that it is confined entirely in real space. The recursion method requires a basis of representation in which the Hamiltonian is sparse. The tight-binding linearized muffin-tin orbitals (TB-LMTO) method proposed by Andersen *et al* [16–19], is ideally suited for our purpose.

The augmented space recursion was introduced by us to deal with configurational averaging in systems where translational symmetry is broken [15–23]. Random alloys were chosen as prime examples of such systems, surfaces were another. Loss of translational symmetry perpendicular to it is the principle feature of the study of electronic structure of a surface. This aspect has been dealt with by different authors in different ways:

(i) Finite slab calculations, which assume that finite size effects are negligible [24].

(ii) Super-cell calculations, where the translational symmetry is restored, but each super-cell has a replica of the finite system and the assumption is that the super-cells are

large enough so as not to affect one another.

(iii) The slab Green function method where the translational symmetry parallel to the surface is utilized and the perpendicular direction is treated in real space [25,26].

(iv) The fully real space based recursion method [27] which does not require any translational symmetry was originally developed for dealing with surfaces and interfaces.

As we have seen, the overlayers produced by molecular beam epitaxy and other vapor deposition techniques are, by and large, rough. Local probes such as STM techniques reveal steps, islands and pyramid-like structures. Moreover, there is always inter-diffusion between the overlayer and the substrate leading to a disordered alloy-like layer at the interface. This brings in the last important aspect of the problem: roughness or disorder parallel to the surface. A majority of the theoretical work done on surfaces and overlayers so far had always assumed flat layers without inter-diffusion. These generally involve the use of surface Green functions, $G(k_{\parallel}, z)$, which allow breaking of translational symmetry perpendicular to the surface, but presume such symmetry parallel to it [25,28]. Roughness has been introduced in overlayers by randomly alloying it with *empty spheres* [26]. Such alloying have been assumed to be homogeneous and have been treated within a mean field or the coherent potential approximation (CPA). Clustering and short-ranged order are perhaps even more important at surfaces than in the bulk. Attempts at going beyond the CPA has not been generally successful.

Let us now justify why we wish to introduce the augmented space recursion based on the TB-LMTO as an attractive method for the study of rough surfaces, overlayers or interfaces.

The CPA has proven to be an accurate approximation in a very large body of applications. Why then do we wish to go beyond? We should recall that the CPA is *exact* when the local coordination is infinite. Its accuracy is inversely proportional to the local coordination. We therefore expect the CPA to be comparatively less accurate at a surface as compared with the bulk calculations. Further, the CPA basically describes homogeneous randomness. It cannot accurately take into account clustering, short-ranged ordering or local lattice distortions, of the kind we expect to encounter in the rough surfaces produced experimentally. The ASF allows us to describe exactly such situations, without violating the so-called 'herglotz' properties which the approximated averaged Green function must possess [29].

We shall combine the ASF with the recursion method to calculate the configuration averaged Green functions. The recursion method, being entirely in real space, does not require any translational symmetry and is ideally suited for systems with inhomogeneous disorder. However, for the recursion method to be a practicable computational technique, we must choose a basis of representation in which the effective Hamiltonian is sparse, i.e. short ranged in real space. The best choice of a computationally simple yet accurate basis is the TB-LMTO. This is what we describe in this section.

Having produced an atomic model out of the rough surface generated by the coupled equations, we shall consider an extra *tracer* Fe atom and determine its bonding energy at various different sites on the surface. This energy is defined as the difference between the system which consists of the surface with the extra atom bonded at a given site and that of the surface without the tracer atom plus the energy of the isolated tracer atom. Any attempt at calculating these energies separately and then subtracting them leads to very large subtractive errors and hence to non-sensical results. We shall use the orbital peeling technique of Burke which was designed to calculate exactly such energy differences directly.

We have carried simulation of the coupled equation of growth on a two-dimensional surface of dimension 50×50. The profile of $h(\mathbf{x}, t)$ shows a super rough behavior with grooves and mounds. The input potential parameters were prepared first by a super-cell calculation within the TB-LMTO. The unit cell had three Fe layers on nine Ag layers with three empty sphere layers on top in a tetragonal structure. Self-consistent TB-LMTO parameters obtained from these calculations were used as the starting point of our LDA-self-consistent. Nine levels of recursion were used to generate the continued fraction co-efficients. The charge density was generated from the local density of states and the LDA potentials generated from the charge density. We calculated the energy difference between the energies of the systems with (a) an adatom in various sites on the top of the rough surface and (b) without that. The energy difference gives the energy of breaking the bonds of an atom at a particular site before it can diffuse to other sites. According to the Wolf–Villain conjecture, atoms diffuse so as to maximize their number of nearest-neighbor bonds. In other words, the atoms having more bonds have greater lifetimes in their respective sites. We have verified that atoms sitting at larger concave curvatures are easier to detach. The chemical potential is proportional to the local curvature and this leads to the term $\nabla^4 h$ in the coupled equations.

Figure 4 (left) shows the contour plot of the curvature at the top of the height profile at various points over the substrate, as produced by the coupled statistical equations. Figure 4 (right) shows the contours of the binding energy for the tracer atom, again on top of the height profile, as calculated by orbital peeling of the TB-LMTO Hamiltonian. A remarkable similarity of the contour profiles point to the fact that the minimum energy positions of the tracer is at points of highest positive curvature (convex with respect to the substrate) or where the number of nearest neighbors available for bonding is the largest. Figure 6c indicates the relationship between the curvature and the number of nearest-neighbor atoms to bond with. This was the main assumption behind the WV term in the equations, which is thus justified by our energy calculations.

To justify the transfer term, we have picked out positions of varying slope and calculated the energy required to knock out the tracer atom bonded at these slopes. Again the orbital peeling method was used to obtain the energy difference accurately. The calculation showed that it requires less energy to knock off an atom at a sharp mound than in a gentler one. This is a justification for the $\nu|\nabla^2 h|$ term, through which a bonded atom gets knocked off due to local disturbances, either thermally or mechanically, into the cloud of unbonded atoms around the surface.

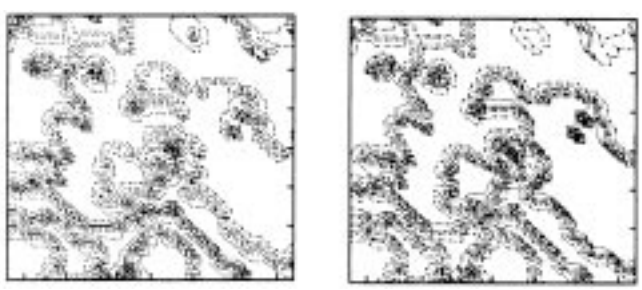

Figure 4. (**Left**) Contour plot of the local curvature of the rough surface. (**Right**) Contour plot of the binding energy of the tracer atom to the surface atom on the rough surface.

The justification of the condensation term in $\mathscr{T}$ is more difficult from simple energetic considerations. However, physically it is reasonable to assume that it must be proportional to the density of the mobile atom cloud just above the surface. Moreover, such condensation or accretion should take place in grooves of high slope. A formal justification of this term would require a dynamical simulation.

Acknowledgement

This work has been done in collaboration with Anita Mehta and Biplab Sanyal, both at the S. N. Bose National Centre, Kolkata.

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