CRYSTAL GROWTH FROM ATOMS

Anuj Goyal (MM05B028)
Mayur Vaidya (MM05B032)
Prahlad Kumar (MM05B015)
Joish Rajendrakumar (EE05B100)
Santosh Raghavan (MM05B019)
Tarun Kasuganti (MM05B024)

Abstract:
In this paper, we aim to describe the growth of crystals from various media, but with an atomic perspective. To start with,we describe thermodynamics of nucleation and nucleation processes. Extensive discussions of various quantities which contribute to crystal growth follow. Models describing crystal growth in FCC crystal have also been covered. Then, the various growth modes and atomic processes involved in crystal growth are elaborated, followed by three case studies, each one describing crystal growth from different media.

Contents:

1. Introduction:

Crystal growth involves a variety of research fields ranging from surface physics, crystallography, solid state elctronics to superconductivity. Although it has been studied extensively more than 100 years, crystal growth has not been still completely understood and plays an important role in both theoretical and experimental research fields, as well as in applications. As the development of scientific instruments and analytical methods, such as x-rays, electron microscopy, NMR, and scanning tuneling microscopy continues, research on crystal growth and structure characterization has entered an atomic level, which makes it possible for further understanding of the physical, chemical, and other properties of the structure nature of various crystals.

The formation of crystalline material may occur from a melt, from a gaseous phase, from a supercritical fluid[1] or from solution.

substrate in solution →generation of supersaturation →nucleation →crystal growth

The growth of a crystal can be stable or unstable and growth mechanism can be layer-by-layer, 2-D nucleation mode, step flow, etc. In this report we will explore some of these aspects by giving the theory and relevant examples.

2. Supersaturation - The Driving Force

A crystalline material is an ordered three-dimensional solid formed by regular repetition of the growth units. The most important requirement for crystallization is supersaturation, which is the driving force for nucleation to occur. Figure 1 shows a typical (super) solubility diagram.

The diagram can be described in terms of three distinct zones:

1. The stable zone of an undersaturated solution where no nucleation or crystal growth is possible. Existing crystals will simply dissolve.

2. The supersaturated metastable zone where growth may occur but spontaneous nucleation does not, and

3. The labile supersaturated zone of spontaneous and rapid nucleation.

---

[1]A supercritical fluid is one which is lies at a point above its critical temperature and critical pressure and cannot be differentiated into liquid and vapour but has properties of both.

Figure 1: The super-solubility diagram
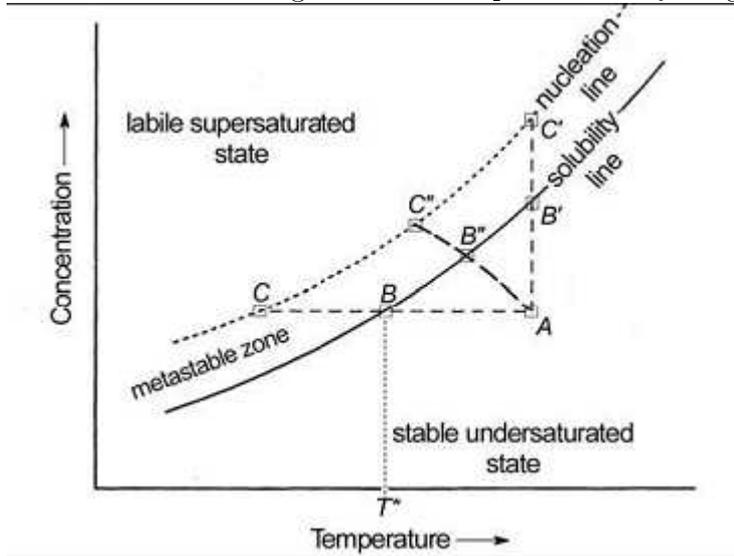
The formation of a supersaturated solution is a prerequisite for crystallization to occur. Supersaturation can be reached by e.g.

- Cooling a saturated solution (corresponding to line AC in Figure 1),

- Concentrating a saturated solution by evaporation of solvent (corresponding to line AC'), or

- A combination of cooling and evaporation (corresponding to line AC").

The following quantities are often used to define the state of supersaturation:

- Supercooling: $\Delta T = T^* - T$ (wherein T^* is the dissolution temperature, T is the actual temperature and $T^* > $ T)

- Concentration driving force: $\Delta c = c - c^*$ (wherein c is the actual concentration, c^* is the equilibrium dissolution concentration at a given temperature (at point B in Figure 1) and $c > c^*$).

- $\sigma = \frac{\Delta c}{c}$ called the relative supersaturation.

3. Nucleation:

Nucleation is the first stage in the crystallization process. Simply defined, it represents the birth of a new crystal. Primary nucleation is believed to

3

be initiated in a series of bimolecular collisions that forms an aggregate of a small number of molecules ('embryos') of the dissolved material.

Embryos below a critical cluster size (rc), are unstable and may disintegrate, whereas embryos that exceed this critical cluster size will become stable nuclei and will grow. One should keep in mind that the size of these embryos is still beyond the limit of detection, even by dynamic light scattering. Consequently, an apparently optically clear supersaturated solution may invariably contain seeds. Therefore, prolonged heating is advisory to ensure total dissolution.
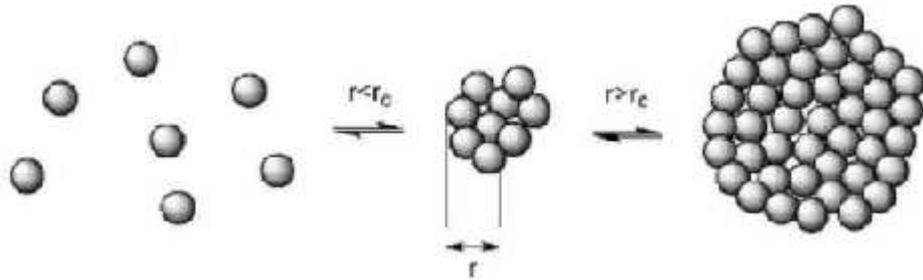
Classical nucleation theory states that the change in the Gibbs free energy (ΔG) required to form a nucleus of radius r is given by the equation below:

$$\Delta G(r) = -\left(\frac{4\pi r^3}{3\Omega}\right) k_B T \ln\left(1 + \sigma\right) + 4\pi r^2 \gamma$$

Wherein: r : size of the cluster, Ω : specific volume of a growth unit γ : solid-liquid interfacial energy k_B : Boltzmann constant σ : relative supersaturation

The first term in this equation is a bulk term (ΔG_V), which is negative and decreases as r^3, and the second term is a surface term (ΔG_S), which is positive and increases as r^2.

Gibbs free energy change of nucleation as a function of the cluster size:

As can be seen in Figure 2, as result of the surface and volume term the ΔG passes through a maximum, denoted as ΔG^*. Taking the derivative with respect to r and setting this equal to zero allows calculation of r_c. This value of r_c is called the critical cluster size.

$$r_c = \frac{2\Omega\gamma}{k_B \ln(1 + \sigma)}$$

Inserting this value of r_c into the original equation yields the activation energy necessary to form a nucleus of the critical size

Figure 2: plot of Gibb's free energy v/s cluster size
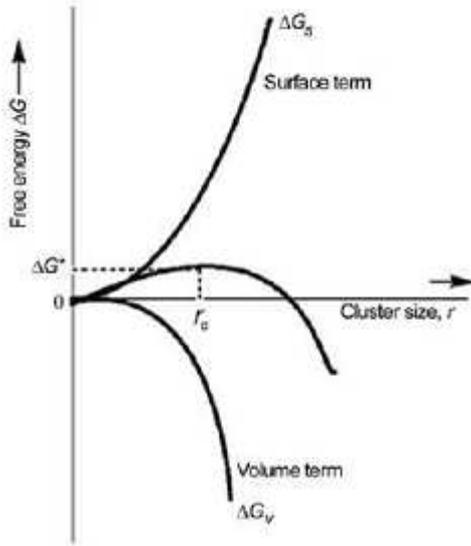
$$\Delta G^* = \frac{16\pi\Omega^2\gamma^3}{3\left[k_BT\ln\left(1+\sigma\right)\right]^2}$$

As the supersaturation increases, both the barrier for the critical activation energy and the value of the critical size decrease. Eventually, as the degree of supersaturation increases, the activation energy becomes so low that spontaneous and rapid nucleation occurs.

The rate of nuclei formation (J), defined as the number of clusters that grow further than the critical size and so become crystals, is given by the equation

$$J = J_0\exp\left(-\frac{\Delta G^*}{k_BT}\right)$$

Since the activation energy is a decreasing function of the supersaturation, the rate of nucleation increases with the increase of the supersaturation. A large rate of nucleation is accompanied by a τ_i small value.

4. Fundamentals of Crystal Growth

Once an ordered structure is formed by nucleation, the growth units (atoms, ions or molecules) can diffuse from the surrounding supersaturated solution

Figure 3: Incorporation of crystal forming elements on the surface of a growing crystal
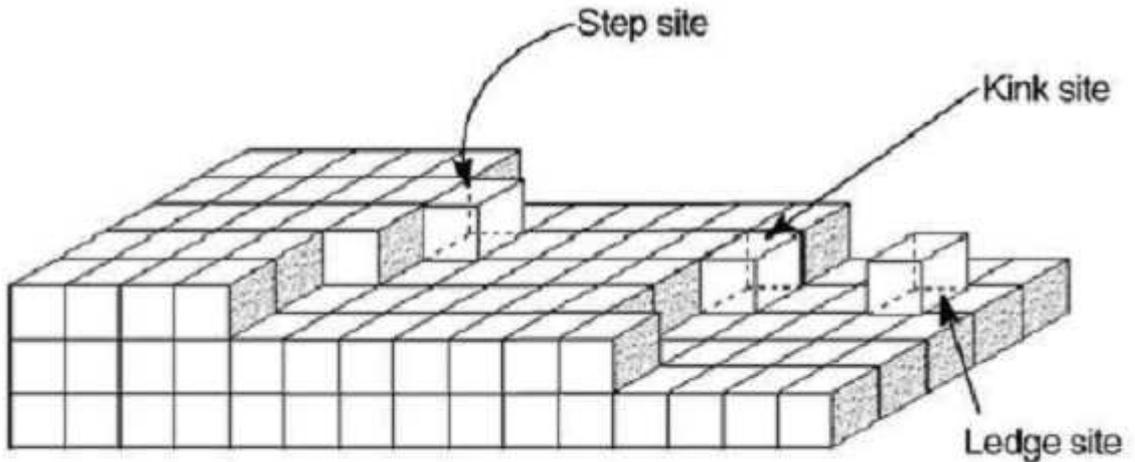
to the surface of the nuclei and incorporate into the lattice resulting in crystal growth. A graphical representation of the crystal growth mechanism is shown in figure 3. This schematic simple cubic crystal used for illustration is referred to as a Kossel crystal. As indicated, adsorption of the crystal forming elements (depicted as a cube) on the surface structure of a growing crystal may occur at three possible sites:

1. *Ledge* sites (incorporation at a flat surface (terrace) having only one site of intermolecular interaction available),

2. *Step* sites (incorporation at a surface having two sites of intermolecular interactions available), or

3. *Kink* sites (three possible sites of intermolecular interactions).

Because crystal forming elements with the highest coordination number are bound most strongly to the surface, incorporation at a kink site will be the most energetically favorable. Furthermore, since incorporation at a kink site will provide a new kink site, the kink site is thus a 'repeatable step' in the formation of the crystal.

Crystal growth can follow two possible mechanisms in solutions:

- spiral growth at screw-dislocations or

- two-dimensional nucleation.

Two-dimensional Growth:

In two-dimensional growth, before grow can occur, a monolayer island nucleus, usually called a 'two-dimensional nucleus', must come into existence on an existing layer (Figure 4(a)). This island becomes the source of new steps and kink sites at which additional units can join the surface. Subsequent crystal forming elements will tend to incorporate at sites where attractive forces are greatest, i.e. they will migrate towards the energetically favorable kink sites (Figure 4(b)). The step-growth will advance until the whole plane is completed (Figure 4(c)) and a new two-dimensional nucleus has to be generated before growth can advance. This two-dimensional growth mechanism is also known as the 'birth and spread' model[9]; after nucleation (birth) of a monolayer island it can grow (spread) laterally across the surface. Two-dimensional growth is only expected to occur at relatively higher supersaturation since it is difficult to generate a nucleus on an already existing flat crystal surface.

It has also been derived- thermodynamically, that for $\alpha > 1$ [2] the shape of a step is a loop that encloses monolayer of molecules and for $\alpha < 1$ the loop encloses a hole and is surrounded by monolayer of molecules. The shape is as shown in figure 5. [3]

This shape turns out to be independant of α but its size does depend on it. At lower temperatures, the shape becomes more like a square side l'. In case of a dislocation of the screw type, under over saturation, the step which is curved and extends between two dislocations of opposite signs, is a part of the structure of critical nucleus of the corresponding size. There are two possibilities but one of them is unstable as shown in figure 5.

Spiral growth from screw dislocation:

It is necessary to have a model that describes growth at low supersaturations, since two-dimensional growth only occurs at high supersaturations. At low supersaturation, growth occurs along screw dislocations (Burton-Cabrera-Frank (BCF) model). This model (Figure 6) is based on a defect in the structure of the crystal lattice formed by stress inside the crystal lattice, which produces spiraling mounds. These steps of monomolecular height provide energetically favorable positions for further deposition, comparable to kink sites in the two-dimensional growth model. It can be seen that these screw dislocations in the crystal are a continuous source of new steps and that this screw mechanism provides a way for steps to grow uninterrupted.

---

[2]α is the degree of supersaturation and $\alpha = 1$ at perfect saturation (equilibrum)

Figure 4: 2-D nucleation - (a) formation of 2-D nucleus, (b) migration of ataoms towards kink sites, (c) completion of the layer
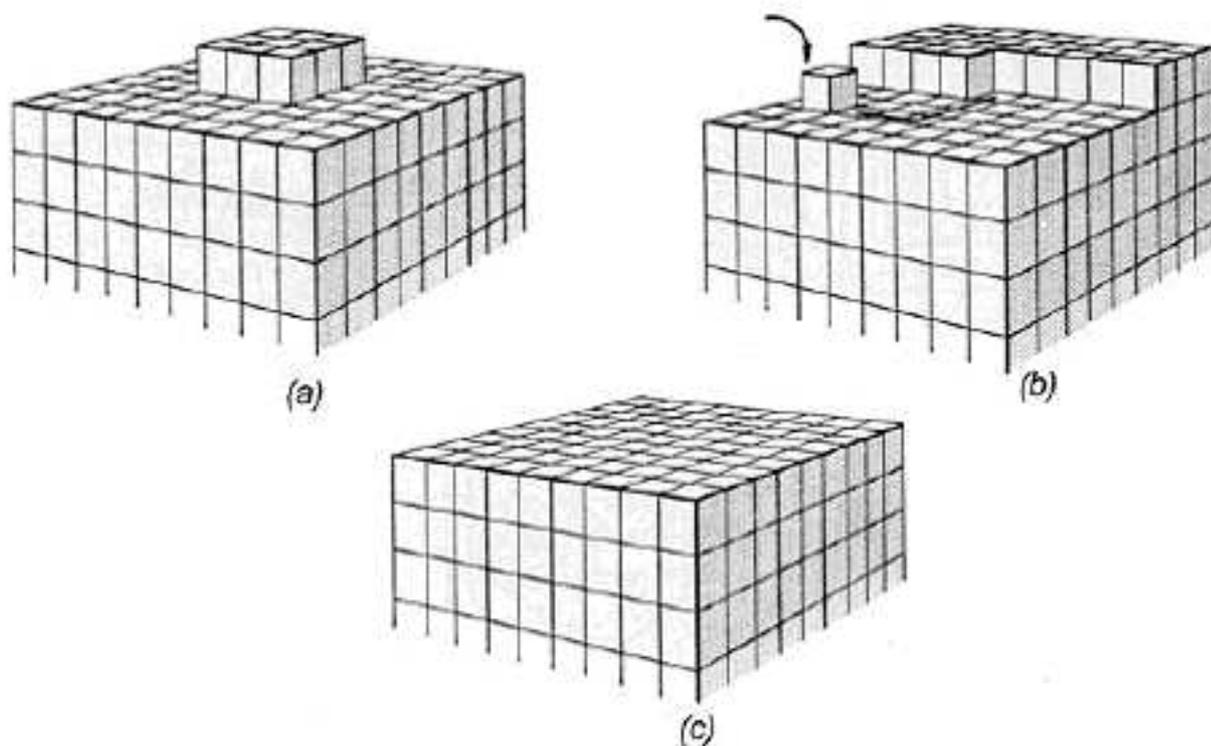
Figure 5: (left) Structure of a 2-D nucleus at its critical size - l' is the size of the square if critical nucleus is approximated to a square (right) Equlibrium positions of a step between 2 dislocations P and Q: PAQ is stable but PBQ is not.
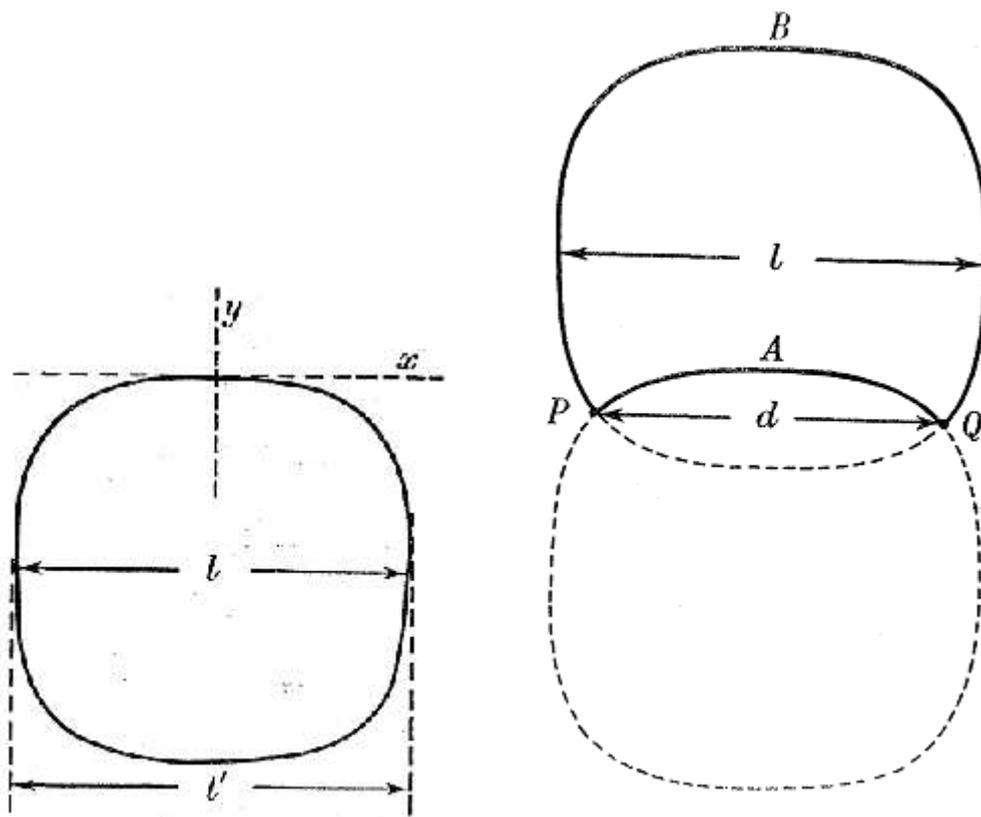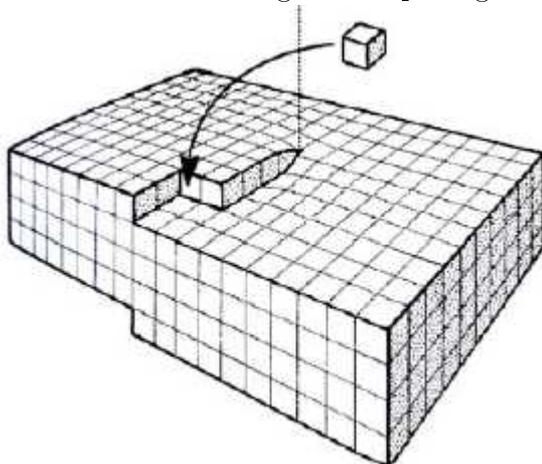
Figure 6: Spiral growth from a screw.

Therefore a lower degree of supersaturation is required than for the two-dimensional nucleation.

Crystal Habit

The crystal habit, or morphology, is the external shape of a crystal and is governed by the different rates of growth of the various faces that bound the crystal. The growth of certain faces may be preferred over others and the shape of the growing crystals will be determined by the presence or absence of dominant growth directions. Crystals that grow nearly uniformly in all three dimensions will become cubic. If the crystals grow mainly along one plane, the habit will become tabular or plate-like. Finally, if the crystal grows mainly in one direction it will assume a needle-like form. In general, the *slowest growing faces* are those that determine the habit.

Since many chemical processes rely on the isolation of the final product by crystallization, the control of crystal size and their size distribution is important since this will determine the ease and efficiency with which the crystals can be separated by filtration or centrifugation. Crystals that are needle-like in shape tend to pack as impervious layers and cause problems in filtration, whereas crystals with cubic habits result in layers that filter well. The habit of a crystal can vary depending on the environment in which it is grown. A number of factors can affect the habit of a crystal. These include solvent, pH, impurities, supersaturation, and temperature.

Figure 7: Effect of adsorption of additives or impurities on layer growth.
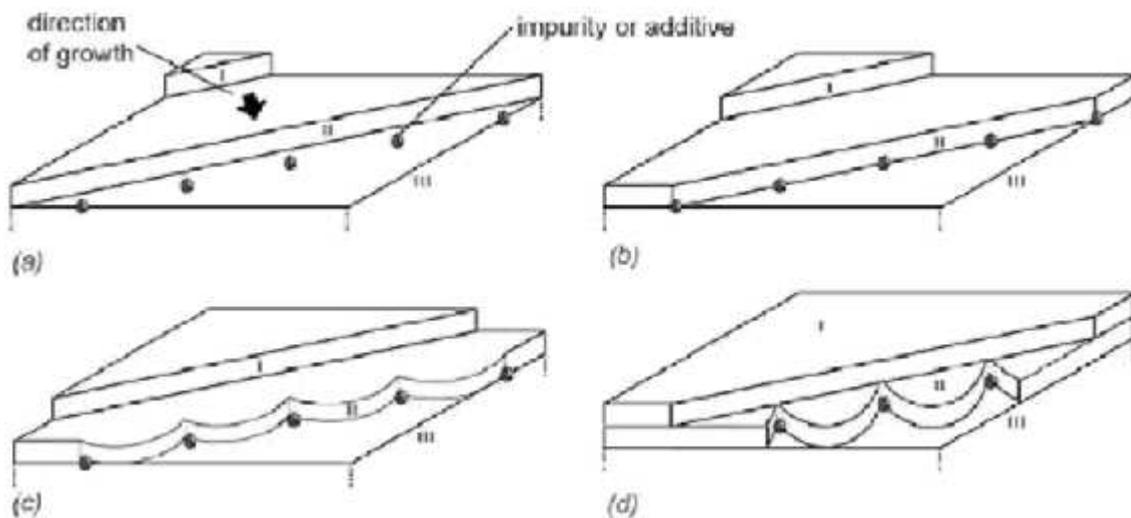
Habit Modifiers

Habit modifiers, either present as impurities or added deliberately, have a profound effect on growth rate of one or more faces, even at very low concentrations. These impurities can be any substance other than the material being crystallized. Therefore even the solvent from which the crystals are grown can be considered to be an impurity. If impurities are deliberately added to produce a desired morphological change, they are referred to as 'additives'. By adsorbing on specific faces, impurities or additives can retard and eventually even stop growth. In Figure 7 the step mechanism of growth of two layers at a surface is depicted schematically. In this cross section, layer I grows on top of the lower positioned layer II, and layer II grows in the same direction on the lower positioned layer III. From the surrounding supersaturated solution the crystal forming elements adsorb on the surface and the layers grow in the indicated direction and the rate of growth depends on the relative rates of separation and incorporation.

When impurities or additives become strongly adsorbed on a growing surface (e.g. layer III, Figure 7a), the growth of layer II adjacent to such sites is retarded and eventually can stop completely (Figure 7b-d). Subsequently, the growth of layer I will be inhibited (Figure 7d). Because the "concentration" of active growth sites is so low, very low concentrations of impurities or additives can retard or stop further growth. Once a certain level of supersaturation is reached, the additive is either released or the additive will be overgrown and becomes incorporated in the crystal. Urea and hex-

11

acyanoferrate(II) are known habit modifiers in the crystallization of sodium chloride. In pure solution (without a modifier), sodium chloride crystallizes with a cubic habit. In the presence of only 1 ppm urea, crystals of sodium chloride are obtained with an octahedral habit. In the presence of 1 ppm hexacyanoferrate(II) the habit changes to a dendritic habit[9].

Special cases of additives are 'tailor-made additives'. These man-made additives closely resemble the chemical structure of the crystallizing solute and are designed to adsorb or incorporate selectively into the lattice on specific crystal faces to produce a desired morphological change.

5. Atomic model growth in FCC crystal:

A particular cluster is better than any other as a seed for macroscopic crystal growth if it has the ability to grow fast, and leave the sub-critical size region before disintegration. Clusters with low surface energy will not have this property since the surface will have fewer nucleation sites. Other clusters will grow until the nucleation sites are all occupied. So the challenge is to make sure that the nucleation sites are never exhausted.

2-D model

The Wulff theorem says that the equilibrium shape of a crystal minimizes the total surface area at constant volume. As a result of this, the crystal will have low index planes at the surface. Prominent among these will be the closely packed (111)-faces and the not so closely packed (100)-faces. The vacant sites on the (111)-face are 3-coordinated whereas the ones in the (100)-face are 4-coordinated. So the (100)-face will grow faster. Since all sites on the (100) face will be filled, it will be in correct registry. The (100) nucleus will spread over the supporting face by step- flow. The new layer formed will not extend over the edges to grow over adjacent (111)-face, which is possible on the surface of a Mackay Icosahedron. In fact, the formation of a new (100) layer causes a reduction in the total (100) surface area, and increases the (111) surface area. In contrast to the (100) growth, the (111) layer formed will be out of registry. This is because, not all of the available sites will be occupied, and atoms in the nucleus are in wrong sites, and a stacking fault occurs[8].

Under conditions of near-equilibrium, the observed growth rates are much greater than those possible with the slowly growing, close packed (111) planes. Frank suggested that surface nucleation could be avoided if the surface contained a step, which is comparable to the border of an incomplete

layer, except that the step cannot be annihilated when the layer is finished. A step can be created when a screw dislocation travels to the surface of a crystal. But there exists another method to achieve step-growth in an fcc-crystal. Here stacking faults are introduced to reduce the difference in growth rates of (100) and (111) faces. In a perfect crystal (a, c) the stacking-order is ABCABC in all sets, and the surface is atomically flat. If one set contains a single hcp stacking-fault CACA the surface will exhibit a step (b); this is obvious by thinking of the fault as resulting from the removal of a single layer (B in Fig. 1a) from a perfect crystal; the gap can be closed by pushing the crystal-halves together in the direction of the arrows, in order to make the A- and C-layers fit. The step-height is $1/3$ d_{111}, since it requires three layers to be removed to obtain a full step. Step- and kink-sites are 4- and 5-coordinated, rather than 5- and 6-coordinated as in a full step. Obviously, a non-integral step in an (111)-face betrays a stacking-fault in one of the 3 sets of close-packed layers not parallel to the surface. Conversely, an atomically flat (111)-face guarantees the absence of such defects, which suggests that stacking-faults could be prevented when the edge-atoms of successive layers could be forced to be in the same plane. This is exactly what the surface-step does, as is illustrated by Fig. 8d. In the situation in Figure 8d, nucleation will start with the growth of C layer in the right hand direction, above the A layer. This creates a new step with opposite step direction, and height $2/3$ d_{111} over the old one. This starts the growth of a C layer towards the left, and so on. The steps stimulate the deposition of monolayers in correct registry, i.e. they may be responsible for the observed stacking-order ABC in fcc crystals.

3D model

A perfect fcc crystal may be in the shape of a regular octahedron, bounded exclusively by close-packed (111)-faces. To achieve a good enough growth rate in all directions, we need steps in all directions. This is possible if there are 4 differently oriented screw dislocations or 2 crossing stacking-faults. In the case of screw dislocations, the strain generated cannot be withstood by small crystals and clusters, and causes disintegration. Stacking faults can be easily added to small clusters, with not much effect on the cohesive energy. The smallest structure with two crossing stacking faults is shown in Figure9. It is a 22-atom cluster, consisting of two identical, incomplete, 11-atom hcp anticuboctahedra[8]. It has nucleation sites that are both 3 and 4 coordinated. This also exists in the perfect fcc cuboctahedron. The difference lies in that, when a vacant site is occupied, it creates new sites that are 4 and 5 coordinated. This makes sure that the nucleation sites are

13

Figure 8: Systematic arrangement of close packed layers below the surface in fcc (a-d) and hcp (e-f) crystals.
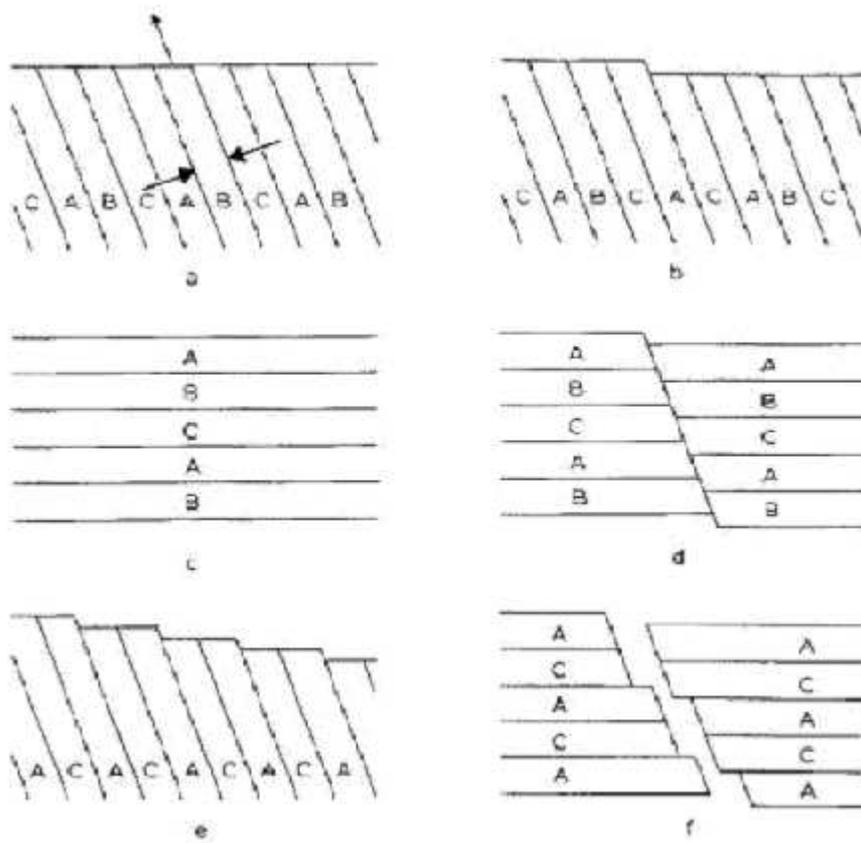
Figure 9: Two views of a 22-atom cluster that supports fcc growth. The cluster is a twin, whose individuals (distinguished by shading) are incomplete 11-atom hcp anti-cuboctahedra, with two neighboring atoms removed from the central hexagonal ring. The exposed 4-coordinated sites can not be exhausted by occupation, as occurs with a perfect fcc cluster. A vacancy-channel is visible in the right drawing.
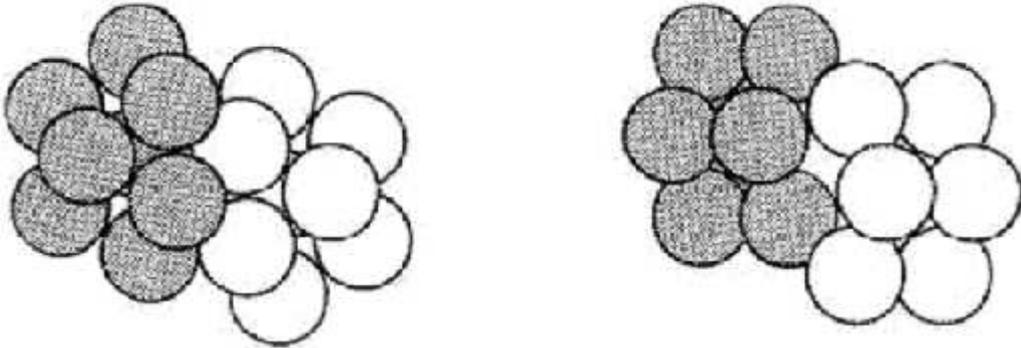
not exhausted. It is possible to model ordered isotropic growth into a nearly perfect fcc crystal with only two stacking faults, if one starts with a 22-atom cluster.

6. Crystal growth modes and atomic processes:

Here we consider a very widely used way of growth called Epitaxy. *Epitaxy* is the phenomenon of ordered crystalline growth on a monocrystalline substrate. Here, the substrate acts as a seed crystal, where the deposited film takes on a lattice structure and orientation identical to those of the substrate. Epitaxy is mainly of three types, *Heteroepitaxy, Homoepitaxy* and *Heterotopotaxy*. While Homoepitaxy deals with growth of a crystal on a substrate made of the same material as that of the growing substance, Heteroepitaxy deals with growth of a crystal on a substrate made different material. Heterotopotaxy is similar to Heteroepitaxy except for the fact that here, thin film growth is not limited to two dimensional growth. Here the substrate is similar only in structure to the thin film material.

Growth of crystals can be classified broadly into two types, mainly, *Stable and Unstable growth*. We first consider Stable growth as it is comparatively easy to understand. Unstable growth mostly deals with the kinetics of crystal growth on which we will not emphasize much. The term, *Stable Growth* itself is enough to visualize the picture of a planar or a quasi planar surface or a

solidification front, moving along the direction of growth of the crystal. We know that every surface has its own chemical potential, μ. If there exists an equilibrium between the crystal and the vapour (or melt/solution), then they have the same chemical potentialμ_{eq}, hence the velocity of growth of the crystal, v vanishes. The difference $\Delta\mu = \mu - \mu_{eq}$ is the driving force for crystal growth. For Vapour growth, generally Molecular Beam Epitaxy (MBE) is considered to be a close and relevant example. Molecular Beam Epitaxy is growth of crystals by shining a stream or ray of molecules moving in the same general direction, usually in a vacuum, called a *Molecular Beam* on a substrate. In the case of MBE the vapour is replaced by a beam, whose directionality implies a more severe sort of disequilibrium than that given by $\Delta\mu$ only. If an appropriate average over beam directions is taken, the MBE case becomes identical to the vapour case (with $\Delta\mu$ very large). We usually assume that the vapour is treated as an ideal gas, the vapour density and pressure will be proportional to the absolute activity, $z = exp(\beta\mu)$(where $\beta = 1/k_B T$, k_B being the Boltzmann constant, and T, the temperature). It it also important to note that the rate of detachment in forms of desorption or evaporation from the surface of the growing crystal is generally very minimal in case of MBE.Hence $\Delta\mu \rightarrow$ inf, the driving force is so high that diffusion can be easily neglected. Hence it constitutes pure growth mechanism. The case of MBE also provides high $\Delta\mu$, not as high as the latter case, but high enough to neglect diffusion.

Different Growth Modes:

While studying crystal growth, we normally come across different growth modes of crystals. Different growth modes we normally encounter are layer-by-layer growth mode, three dimensional growth mode and an intermediate mode called Stranski-Krastanov mode. They are explained below in some detail.

Layer-by-layer is the mode in which one crystal layer is preferred to have completely formed before moving on to formation of another layer on top of it. (Figure 10a). But some problem arises in this mechanism due to kinetics associated with this mode because of random supply of atoms to the growing crystal layer. However this problem is not observed in MBE growth due to constant and unidirectional supply of molecules to the growing layer at a constant speed, overcoming all the difficulties faced by nucleation and unfavourable kinetics.

Another growth mode is called, *Three Dimensional Growth* mode which is opposite to the previous mode. In this mode, many crystal layers grow at the same time: the atoms, depositing over relatively high layers, cause the

Figure 10: Different growth modes: ((a) Layer-by Layer, (b) 3-D growth (c) Stranski Krastanov mode
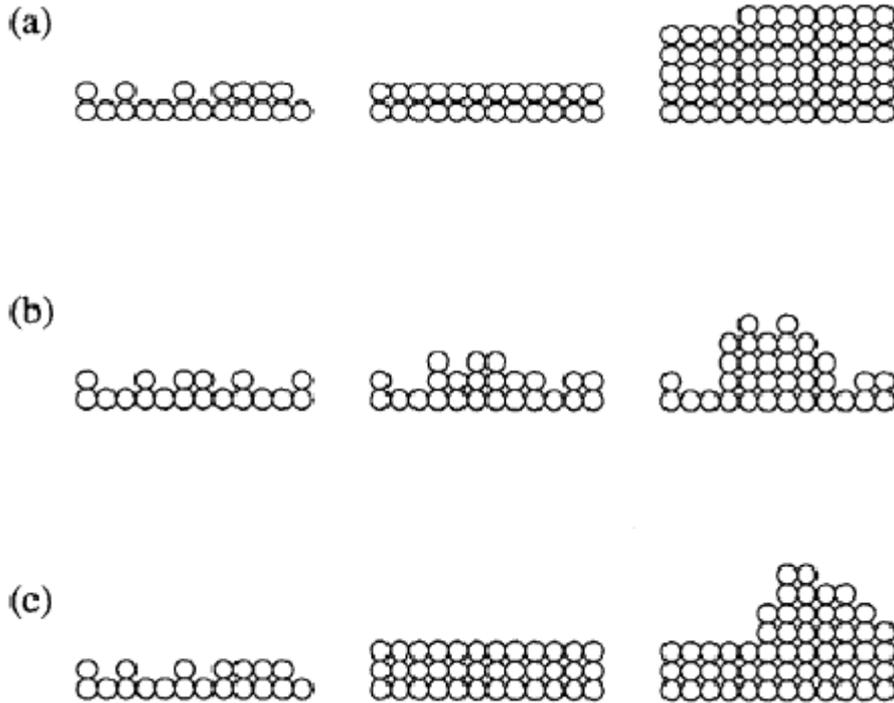
surface to form hillocks and cavities (Figure 10b)

The third possible mode is that of *Stranski-Krastanov growth* mode where atoms initially form crystal layers on a substrate in the layer-by-layer mode. But after a few number of layers, the growth mode shifts to three dimensional growth mode. (figure 10c)

In the case of growth of crystal from MBE process, the three dimensional growth occurs at low temperatures due to its far from equilibrium nature, owing to its high driving force. But this growth mode shifts to layer-by-layer mode when the temperatures are high. This is due to the fact that at high temperatures, the atoms have sufficient energy to cross local energy barriers (also called, *Ehrlich-Schwoebel barriers* [2](ES barrier)) which obstruct them from climbing down high energy step edges otherwise. High temperatures guarantee sufficient diffusion to happen between layers so that the growth of the crystal occurs with a smooth surface without any bumps. But there exist cases where the adatoms are mobile but the barriers at step edges are so high that they are unable to overcome these forces. In such cases, the growth occurs in a special way forming large, ordered features like a pyramid.

Now let us look at cases near equilibrium condition. In these cases, there exists a transition temperature T_R , called Roughening transition temperature. A planar surface turns into a rough surface as soon as the temperature reaches T_R, i.e. it stays smooth below T_R and turns rough above T_R. Recent studies have also proved a growth mode called, *Stepped mode* growth process where there exists an array of steps which are formed and each layer grows horizontally at the same speed and the crystal grows as the step advances over the lower terrace.

One more thing to be explored is the region between the growing crystal and the substrate. There can be an interchange between the substrate and the crystal atoms. And this is due to the low surface tension at this separating interface. Because of this low surface tension, the substrate atoms move out of their lattice and act as a surfactant, facilitating layer growth.

7. Case Study I - Growth from Vapour Phase :

It has been recently found that growth in MBE being unstable, the process forms pyramidal structures which are formed and as time proceeds, many small pyramids which are formed merge, thus increasing the average size of the mounds with time. The existence of such structures is due the presence of the local energy barrier near the step edge, which cannot be surpassed very easily, thus suppressing inter-layer transport. Let us pursue this field of growth of crystals in MBE process.

We can study inter-surface diffusion by taking into account the lateral flux of growth of crystal i.e, the growth along the surface by movement along the surface itself. Take for instance, the flux at the corner of the two surfaces and flux at a very large distance from the corner on (0 0 1) plane as shown in fgure 11.

It is seen in the diagram above fgure 11, a layer of crystal formed on a substrate. When the growing atoms diffuse from a side facet to a top facet, we see the decreasing tendency of the distribution since the atoms diffusing in lateral direction are incorporated one by one on the top facet and finally all atoms entered from the side facet are consumed. On the other hand, when the growing atoms diffuse in the opposite direction, one sees an increasing tendency in the growth rate distribution. It has been shown experimentally that the diffusion direction depends on the vapour pressure of the group V element present in the chamber. The element used here is Arsenic and the element for crystal growth is Gallium.

If we define the ratio of growth rates near the top facet, i.e. at the corner, Rcorner ,and growth rate at a planar surface, far away from the

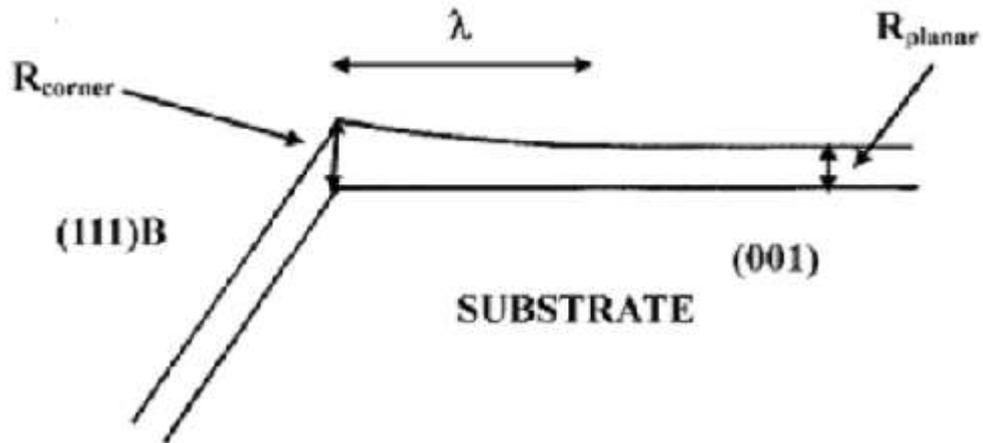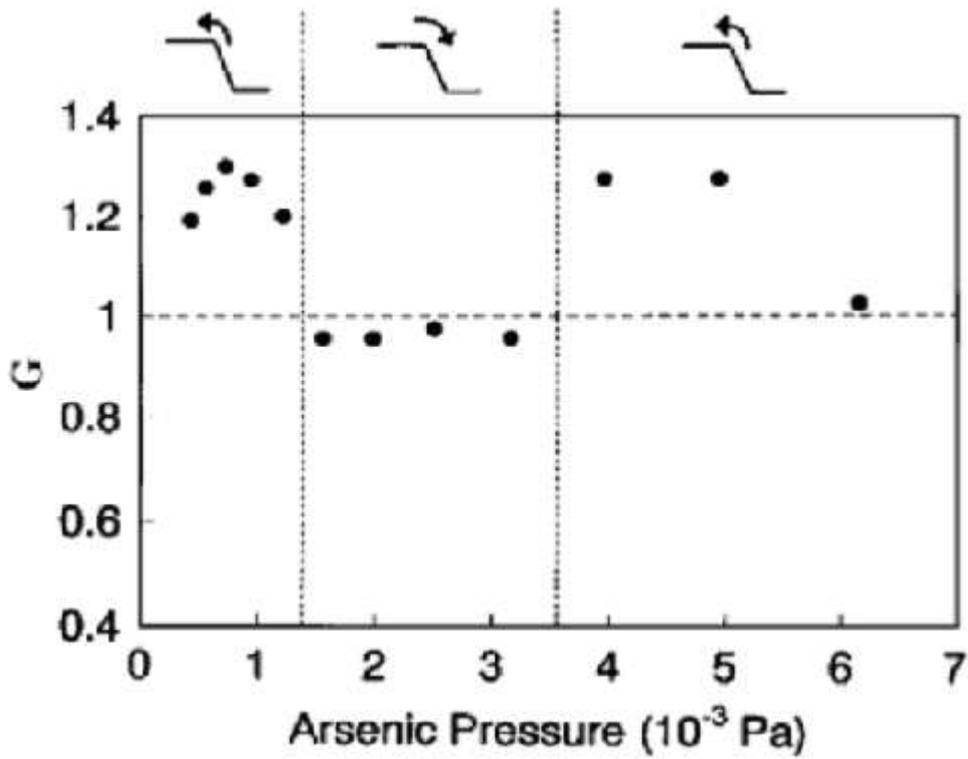Figure 11: Inter-surface diffusion between (0 0 1) and side facet (1 1 1)B

Figure 12: G v/s As pressure - reversal of lateral flux [1]

corner, Rplanar, as G, then the plot of G versus Arsenic Pressure is plotted in figure12. From the figure, we can derivate that at low arsenic pressure, G value is above 1, but as Arsenic pressure increases, G value drops. Hence the direction of diffusion reverses to direction of (0 0 1) to (1 1 1) B. Again, a further increase in the Arsenic pressure again reverses the direction of diffusion.

Inter-surface diffusion occurs if there is a difference in Ga adatom concentrations between two facets. By making use of the directional reversal in lateral flux, one can control the top size of the pyramids during the growth. Figure13 shows the change of GaAs pyramid top as arsenic pressure is changed. When the arsenic pressure is low (1.1×10^{-3}Pa), Ga adatoms diffuse from (1 1 0) facet to (1 1 1) B top facet, while at high arsenic pressure (4.7×10^{-3} Pa), the flow reversal occurs and the sharp top changes to flat top. Thus we can adjust the top size by changing the arsenic pressure. This has extensive use in electronic devices and microstructure fabrication where electron concentration has to be controlled very sharply.

8. Case Study II:Growth from [111] plane of Iridium

Taking the example of atomically smooth (111) plane of Iridium ,we try to examine the atomic events important in the growth of crystals from atoms . Many different atomic process contribute to growth phenomenon of crystal and over layers from the vapour. Major techniques that provide atomic resolution of surface:

1. Field Ion Microscopy.

2. High Resolution scanning TEM.

3. Scanning tunneling microscopy.

Although FCC (111) plane is closed packed plane, but there exists sites of different geometry where Iridium ad-atom can bound themselves. Ad-atom can either occupy the FCC sites at the substrate lattice or they can go to the HCP sites. The binding sites on Iridium (111) plane are mesh like in nature with a diamond shaped unit cell, inside of which and to the left there is occasionally observed an additional ad-atom. In case of ad-atoms sitting on the HCP site on the (111) Iridium plane, the apex points towards right, along [211] direction and the apex points to the left if atom occupies a FCC site .

Figure 13: variation of top of the pyramid due to arsenic pressure variation: (A) initial growth of the pyramid from the mesa structures, (B) pyramids under low pressure with sharp tops ,(C) truncated pyramids under high pressure [1]
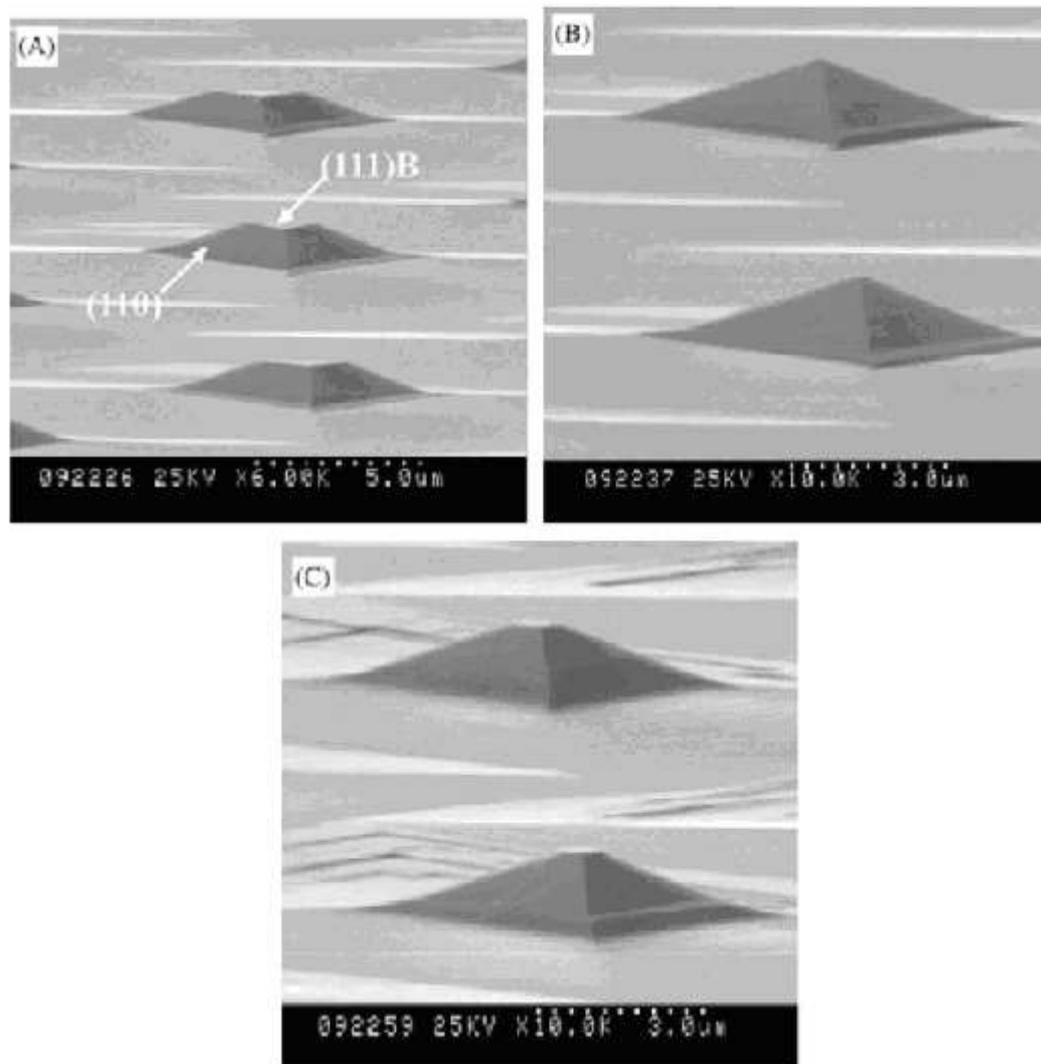
Figure 14: Self-adsorption sites on the (111) plane of the fcc lattice. (a) Hard sphere model with ad atom at hcp site. (b) Schematic, Showing nearest-neighbor distance l and the surface mesh of hcp Sites. All subsequent pictures of (111) are oriented in this way.
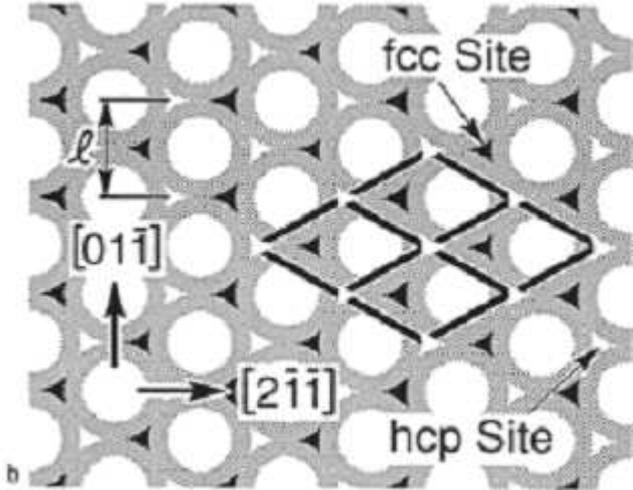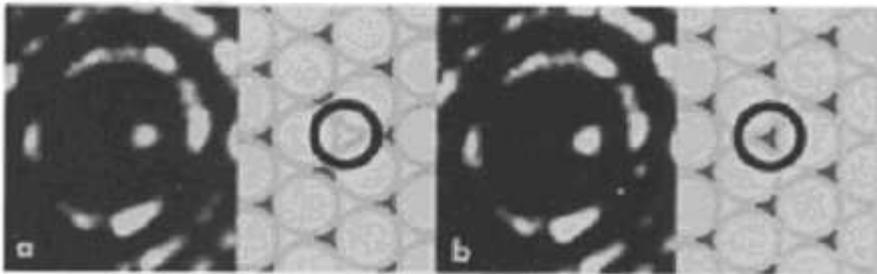

Figure 15: FIM images of iridium adatom at different sites, whose Identity has been determined by mapping . (a) For adatom at hcp site, shown in schematic atri_ght, image is triangular, with apex pointing to the right, along [211]. (b) Ir atom at fcc site. Apex of ad atom image triangle points to left . [5]

Sites at different temperatures

It appears that there is an energy difference between atoms occupying HCP and FCC site. The energy of an atom at a HCP site is about ~ 500 cal/mol [5]lower than at FCC site. Although this difference does not appear large, it is enough to keep the likelihood of an iridium ad-atom occupying the wrong kind of site (that is, an hcp site) at ~50% even at room temperature.

But then question arises that how can an Iridium be grown as FCC crystal from vapour?

From observations it emerges that as growth is a many atom phenomenon, therefore as the size of the clusters increases, its atoms tends to favor FCC sites. After equilibration, heptamers and larger clusters are always found in the right kind of site for an FCC crystal.

Consider deposition of iridium atoms on Iridium (111). The adatoms are bound to the surface with energy of ~6 eV. This condensation energy is much larger than the thermal energy (~ 1/3 eV) of atoms evaporating from a source at 2000 K. How is the energy of condensation dissipated on collision with the surface? If energy transfer is slow, the colliding atom may impart only a fraction of the condensation energy to the lattice on first impact; this energetic adatom may then bound over the surface, covering large distances before eventually coming to equilibrium. This could obviously bring about growth, even at low temperatures. In the opposite extreme, that is if energy transfer is very efficient, the atom will be localized close to the point of impact, and transport to growth sites can then occur only by diffusion under ordinary thermal condition.

The diffusion if Iridium (ad atom on the Ir (111) plane , the process of diffusion takes place in a simple fashion . The ad atoms of Iridium jumps between the nearest neighboring positions with an activation energy ~ 1/20 of the desorption energy. Iridium ad atom displacement is always between nearest neighboring sites. Experiments confirm that Iridium atom movoes from an HCP site to Adjacent FCC site & then back again to nearest neighboring FCC position.

Atomic Incorporation:

During crystal growth , atom diffusing on surface may eventually collide with an ascending step or a descending step. At a ascending step, attractive interaction with neighboring lattice atom establish a deep potential in which atom gets trapped, but incorporation at descending step is marked by two mechanism :
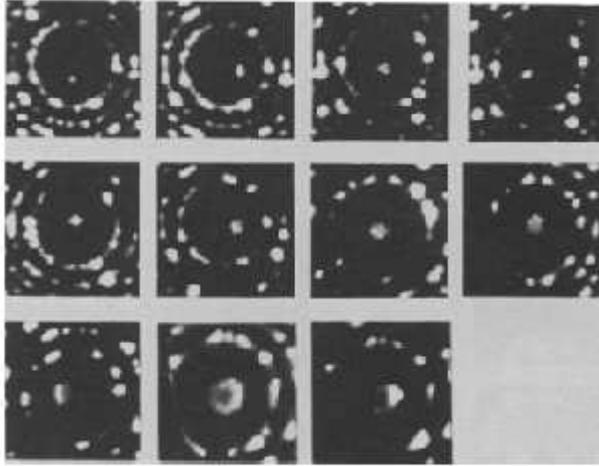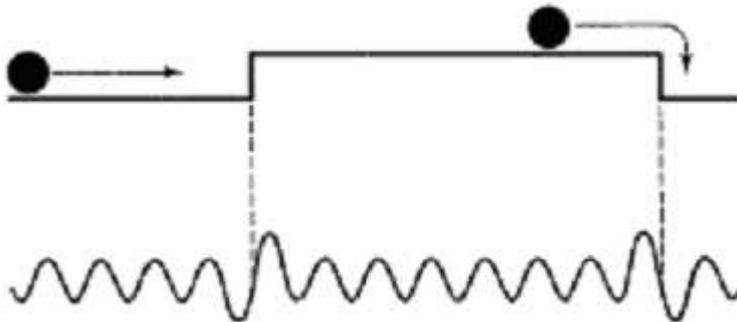
1. Exchange

Figure 16: Cluster formation in Iridium [5]

Figure 17: Schematic illustrating traditional view of atom incorporating at ascending step.

2. Classical jump process.

In incorporation by a exchange the foreign ad atom gets diffused in the cluster lattice & the lattice atom is placed at the step. In the classical jump model, foreign ad atom is placed at the step. It appears that the energetic for incorporation by two mechanisms are not too dissimilar, so that small structural differences favor one over the other.

Atomic incorporation in descending step depends on the clusters size. For the clusters as small as of some 12 atoms, the atom protruding from the cluster after incorporation turn out to be lattice atom , rather than a foreign ad atom placed at the surface. Thus this demonstrates the exchange mechanism in which ad atom pushing the cluster atom to periphery and

Figure 18: Schematic for incorporation of foreign adatom (black) at Descending step by classical jump (top), and by adatom exchanging position with a lattice atom (bottom). The mechanism can be Determined by observing the location of the foreign adatom.
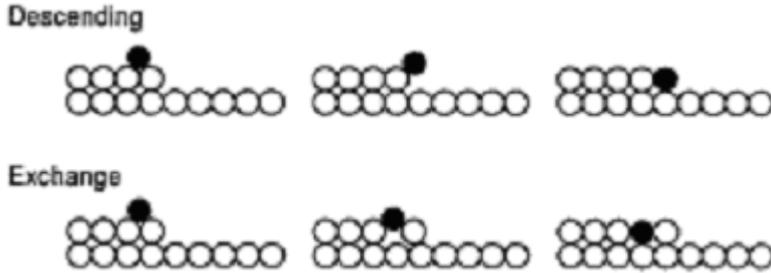

Figure 19: Test of incorporation mechanism for tungsten atom into Ir12 on Ir(111). Left: initial cluster. Center: atom incorporation, after W atom has been deposited on cluster and heated to ~ 220 K; an additional atom is visible at 4 o'clock. Right: additional atom (as well as a neighboring atom) has been removed by field evaporation, but only at voltages characteristic of an iridium atom. [5]
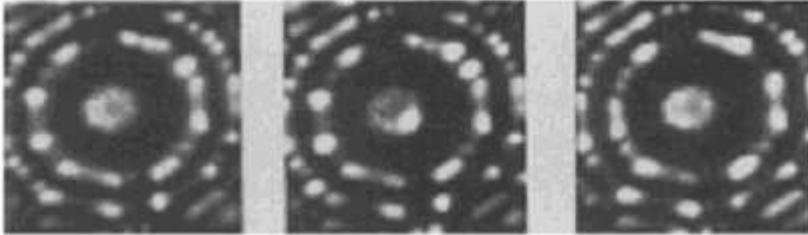

taking its place.

But On a cluster of 50 atoms, mobility of iridium atoms is close to that on a large (111) plane. Thereby when an Iridium atom reaches the edge of the cluster, incorporation is not automatic. Rather, the atom is trapped at the edge, until the temperature is raised appreciably. Then the atom does not return to the more central positions of the cluster; instead, incorporation takes place. The act of incorporation is specific to the geometry of the step and because of the 3-fold symmetry of the (111) plane, the edges of a cluster fall into two categories.

At an edge of type A, which looks like a (100) facet, incorporation requires a temperature of ~ 175 K. and involves classical jump process. At an edge of type B, which resembles a (111) facet, incorporation occurs at significantly

Figure 20: Incorporation of iridium atom at descending step on Irs0 cluster on Ir(lll). Left: Starting cluster. Center: Ir atom incorporates at edge of type A (100 facet) after heating to ˜ 175 K. Right: In a separate experiment, atom incorporates at edge of type B (111 facet) after warming to only ˜ 160 K.
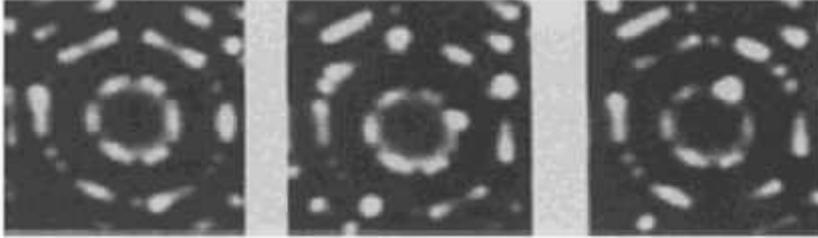
lower temperatures, at ˜ 160 K. and involves atomic exchange.

Observations on Iridium (1 1 1) have been examined at length, and it should be evident that on surfaces of different geometry or chemical constitution, different behavior may be expected. This only serves to emphasize an important conclusion: examinations on the atomic level reveal that the atomic events actually contributing to growth are rather more involved.

9. Case Study III: Growth from Solution

## Atomistic nature of NaCl nucleation at the solid liquid interface:

Computer simulations based on atomistic models have become efficient and powerful approach to study nucleation process at atomistic scale. One such approach uses *Molecular Dynamics* simulations to study nucleation of sodium chloride in a supersaturated aqueous solution.

Determination of Critical Nuclei size:

The determination of critical nucleus size is based on study of probability of decay[3] of a nucleus formed . Now, let us consider the possibility of single atom nuclei [one Na^+ or one Cl^-], for such nuclei, sum of created $Na^+(Cl^-)$ nuclei is 138(110) and sum of decayed nuclei is 74(77). Hence, the probability of decay is $P_{decayNa^+} = \frac{74}{138} = .54 > .5; P_{decayCl^-} = \frac{77}{110} = .7 > .5$. Since the probability of decay is more than that of formation, it cannot be the critical

---

[3]decay refers to detachment of an atom from the nucleus during period of simulation, which in the present case is 1.2 ns

Figure 21: The growth of a two-atom nucleus evolved as a function of time. The Na+ and Cl? ions are represented by purple (smaller) and green (larger) balls. Water molecules are represented by sticks, white for hydrogen, and red for oxygen. The snapshots were taken at (a) t=0.3 ps (300 K), (b) 19.59 ps (300 K), (c) 1200 ps (300 K), and (d) 2550 ps (320 K)[6]
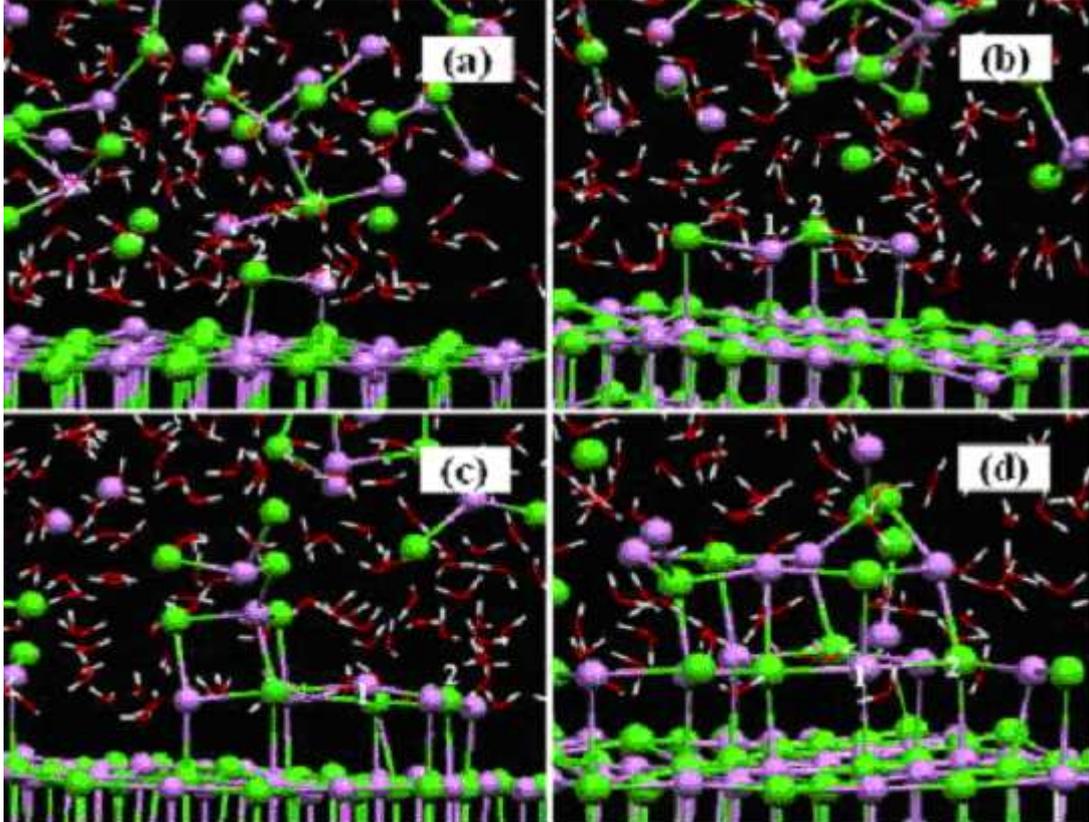

nuclei size. For two atom nuclei, probability of decay, P_{decay2}=.44<.5. This is the critical nucleus size[6]. For a three atom nuclei the probability of decay is still less, .33 which is in accordance with classical nucleation theory.

Snapshots of a typical two atom nucleus at the water NaCl interface are shown in figure21. It evolves from a two atom nuclei to a three dimensional island with increasing size. The maximum coordination ions for the Na^+ and Cl^- in the islands are both six, the same as the bulk case.

Coulombic driving forces for initial nucleation:

The Na+ ions show a higher deposition rate than Cl^-. It suggests that water-NaCl (001) interface is positively charged in the early stages of nucleation.

Figure 22: (a) Top and (b) side views of the water network near the NaCl (001) surface. The snapshot was taken at t=577.5 ps for one side of the NaCl (001). The hydrogen bonds formed between the water molecules are indicated by dotted lines. (c) Time evolution of the average number of hydrogen bond per water at the interface and inside solution. The increasing trend of NHB in solution is due to the continuous nucleation at the interface and inside solution. The decrease/increase of NHB for interface water corresponds to ion deposition/dissolution during the 3D growth mode of NaCl nuclei on NaCl (001)[6]
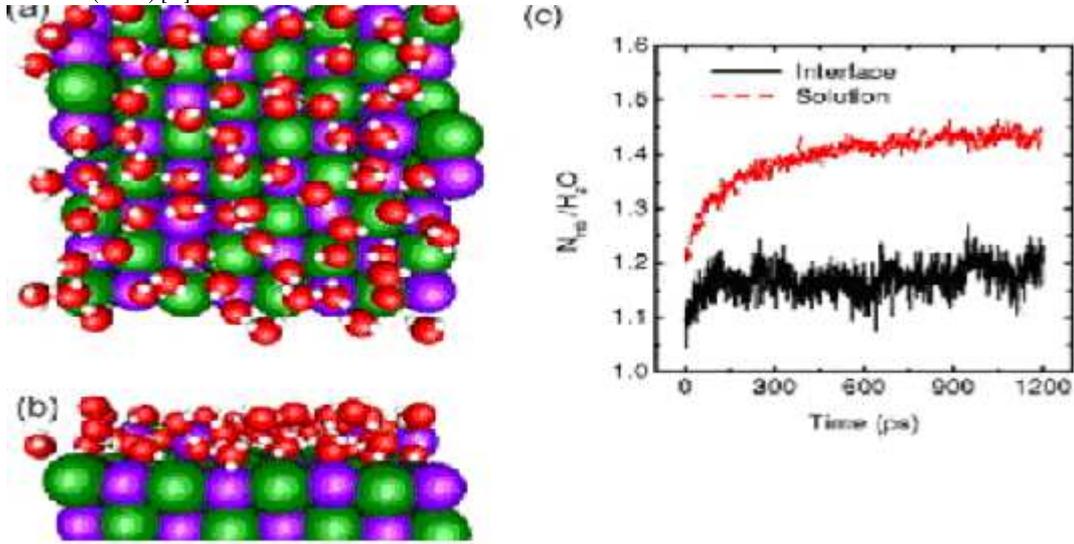
The accumulation of positive charge at the interface will attract the Cl^- ions to deposit on to the seed crystal. This may serve as another driving force for nucleation from the solution in addition to the chemical potential difference in the classical nucleation. The difference in deposition rates is due to the presence of a relatively stable water network on NaCl (001) surface and the difference in hydration force. When the solute Na^+ ions approach the NaCl (001), most of them will replace the water molecules atop the Cl^- at the water-NaCl (001) interface because of the Coulombic interaction between Na^+ and Cl^- ions, and similarly Cl^- ions also undergo the same process. But the $H-Cl^-$ hydrogen bond is much weaker than the $O-Na^+$ interaction. Thus the water molecules adsorbed on the top sites of the surface Na^+ are more stable than the ones adsorbed atop the surface Cl^-. Also the deposition flux of Na^+ is more than that of Cl^- because of its smaller molecular mass.

Conclusion:

There is little or no experimental data available on the atomic configurations near the critical nucleus size, where clusters are more likely to grow than to shrink. Even high-resolution TEM can usually detect only those clusters exceeding about 2 nm in diameter, whereas the critical nucleus might consist of only two or three atoms. It has been recently shown that high-angle annular dark-field imaging in a scanning TEM (HAADF-STEM) is capable of resolving and identifying individual atoms of size near 0.2 nm in diameter[7]. This might prove to be major breakthrough in the atomic study of crystal growth.

Bibliography

[1] Tatau Nishinaga, *Journal of Crystal Growth* 275 (2005) 19-28

[2] Andrea C Levi and Miroslav Kotrla, J. Phys.: Condens. Matter 9 (1997) 299-344

[3] W. K. Burton, N. Cabrera, F. C. Frank, *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*, Vol. 243, No. 866. (Jun. 12, 1951), pp. 299-358.

[4] Tatau Nishinaga, *Progress in Crystal Growth and Characterization of Materials* 48/49 (2004) 104-122

[5] G. Ehrlich, Appl. Phys. A 55, 403~410 (1992)

[6] Yong Yang, Institute of Physics, Chinese Academy of Sciences, Box 603, Beijing 100080, China; Sheng Meng,Physics Department, Harvard University, Cambridge, Massachusetts 02138, *Atomistic nature of NaCl nucleation at the solid-liquid interface*

[7] Tomas Diaz De La Rubia AND George Gilmer, *Watching Nanoclusters Nucleate*, Nature materials | VOL 1 | OCTOBER 2002

[8] B.W. van de Waal, Z. Phys. D - *Atoms, Molecules and Clusters* 20, 349-352 (1991)

[9] D.A. Porter, K.E. Easterling, *Phase transformations in metals and alloys*, 2nd edition,1992.