Chapter 10

THIN FILM GROWTH PROCESSES

Up to this point this text has focused primarily on materials themselves and not how to produce them. A major aspect of materials science is the control of the kinetic and thermodynamic conditions under which materials are produced to yield specific properties. This chapter and the ones that follow describe some of the ways semiconductor electronic materials are created as thin films. For comparison, the most popular method of production of bulk materials was covered in Chapter 4. Bulk wafers are useful as substrates but are impractical for many applications, especially where alloys are needed. In current technology, thin films constitute most of the active and passive layers that are used in electronic devices.

This chapter covers the common features of all vapor phase thin film growth techniques – the processes by which atoms land on surfaces, move about, leave the surface, and how surface atoms go on to produce complete films. As with other chapters in this book, whole texts have been written on the subject so this treatment reviews only the highlights. Following chapters will cover specific classes of processes. Subjects of this chapter and include adsorption, desorption, surface structure and energy and how they are related to surface diffusion and the evolution of morphology, and adhesion.

10.1 GROWTH PROCESSES

In many of the earlier chapters we have assumed the ability to create a desired series of thin layers on a thick substrate. Usually, when semiconducting, these layers are grown as high-quality single crystals because of the problems with defects described in Chapter 7. As one can tell from the discussion of the devices in Chapter 3, the layers must be very thin, sometimes only a few monolayers, with carefully controlled compositions and doping levels. Therefore, the missing element in the previous chapters is how one can practically produce thin high-quality crystal layers. All of the common growth methods involve one or more phase transformations along the path from an initial state, containers of individual reactants, to a final state – a film of desired composition and structure. It is the details of how these transformations occur that determine the quality of the resulting film. While atoms or molecules may be supplied from solid or liquid phases, the most common approach is to provide them through the vapor phase. Before describing vapor phase methods, it is worth a brief mention of the solid and liquid phase methods.

Solid phase growth is used where only structural phase transformations occur and long-range transport of atoms or removal of product species is not required. This is necessary because in solids atoms cannot move very far and the solid material must serve as its own atom source and sink. Solid phase growth is only applied significantly in current semiconductor processing for crystallization of amorphous materials or solid phase reactions, as in formation of silicides by reaction of a metal with silicon.

An example of crystallization of amorphous material is when a large number of atoms are added to solid semiconductors by ion implantation. In implantation, high-energy impurity atoms strike and penetrate the crystal causing damage to such an extent that it may convert the solid to an amorphous structure. Upon annealing the atoms reorganize to recreate the crystal by adding atoms to the surrounding lightly damaged single crystal one layer at a time. The basic process is shown schematically in Figure 10.1. Because an amorphous solid is not unlike a very viscous liquid, the process of solid-phase growth is not unlike a liquid phase growth in which the driving force for the phase transformation is crystallization. The major difference from an atom's perspective is the reduced atomic mobility in the solid compared to in the liquid. For implants in Si single crystals, solid phase epitaxy (regrowth) produces a better final doped material, when done properly, than a lower-dose implant that does damage but does not amorphize the solid.

In the case of solid-phase reaction to produce a silicide, a polycrystalline metal layer is deposited on a Si wafer. The structure is then heated, typically to between 250 and 650°C, depending upon the silicide to be grown. A reaction occurs at the interface producing the silicide. Once the metal-Si interface is completely covered with silicide (at least locally), continuing the reaction requires diffusion of either the metal or Si atoms through the intervening silicide layer. In most cases a wide variety of silicide compounds may form by reaction with Si. Thus, in the case of Ni, the commonly identified silicides are Ni_3Si, Ni_5Si_2, Ni_2Si, Ni_3Si_2, NiSi, and $NiSi_2$, as may be seen from a Ni-Si binary phase diagram.

With so many silicides to choose from one might then ask which forms first. An obvious possibility is that the most stable silicide (with the highest free energy of

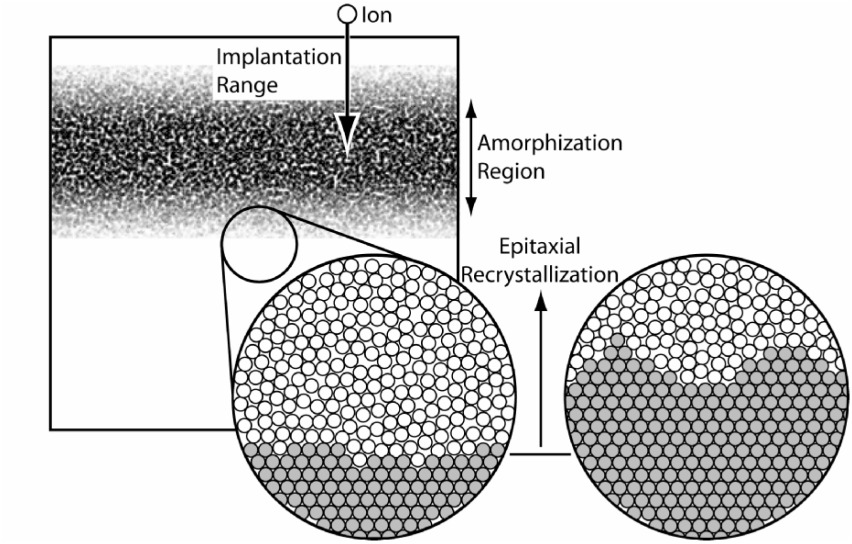


Figure 10.1: Shows the process of regrowth of a crystal from an amorphized region. For example, suppose that the right hand close-up represents the as-implanted material while the right hand close-up is after partial recrystallization. Regrowth of this type can result is a perfect crystal if done correctly.

formation at a given temperature) would nucleate first. However, one also requires reactants to produce a given product phase and low energy interfaces. Although exceptions occur, it turns out that in general the first phase to nucleate in silicide reactions is usually rich in the diffusing species, although it is not always the phase with the largest amount of that material. For example, Ni_2Si is the first phase to nucleate at a Ni-Si junction even though two more Ni-rich phases exist. In this case the Ni_2Si is the most stable (most exothermic heat of formation) of the Ni-rich phases. One may see how the nucleating phase might be rich in the diffusing species if nucleation is dominated by the law of mass action rather than by thermodynamics and if an excess of diffusing reactant accumulates before nucleation can occur.

After a phase is formed the reaction continues, either limited by the reaction rate at the interface where the diffusing species meets the stationary reactant, or limited by transport of the reactant through the silicide. The former does not depend upon the silicide thickness, so the thickness increases linearly with time, and exponentially with temperature (from the reaction rate). Diffusion-limited transport requires increasingly long-range movement the thicker the silicide becomes. Therefore, the rate decreases with increasing silicide thickness and the thickness of the silicide increases as the square root of time and exponentially with temperature (due to the increasing diffusivity). When the film becomes thick enough that reactant transport

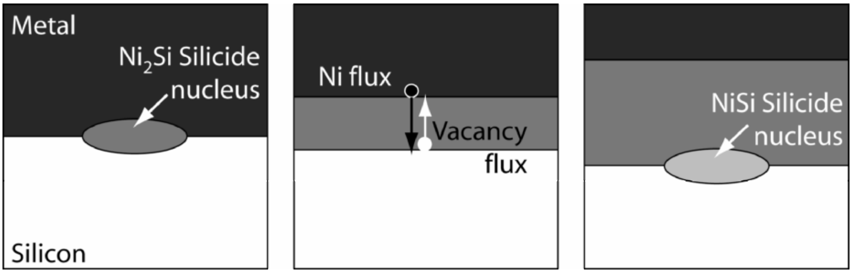


Figure 10.2: Shows the basic reaction process for forming a silicide by solid-phase reaction. A metal is deposited directly on a silicon layer and the couple is heated to permit the reaction. The first event is nucleation of one of the silicide phases. This grows thicker and slower until a new more stable phase has the chance to nucleate.

slows, a second more stable phase, if any, may nucleate. In the case of Ni-Si reactions, this leads eventually to NiSi and $NiSi_2$ formation if sufficient reactants are available. The basic silicide reaction process is shown schematically in Figure 10.2.

An interesting feature of the solid phase reaction to form silicides is that the diffusing reactants move by a vacancy mechanism. For this to occur it is necessary to move vacancies in the opposite direction as do the atoms. Thus vacancies are formed at the interface where reaction is occurring, diffuse through the silicide, and are eliminated at the other surface. However, this elimination does not occur instantly and the vacancies may penetrate a few nanometers into the diffusing reactant layer. When the moving species is Si, this means vacancies are formed at the metal/silicide interface, move to the Si and are eliminated at the Si/silicide interface. Their shallow penetration into the Si substrate can cause anomalously high diffusion of impurities in the Si near this interface, which may affect the doping profile there. When Si is the diffusing species, impurities in the Si, notably As, may be rejected by the silicide. Therefore, as the silicide grows the dopant concentration in the Si in front of the advancing silicide may be enhanced. Preferential incorporation of an impurity in the silicide is observed with other dopants leading to a reduction of dopant concentration in front of the silicide interface. For a detailed discussion of silicide reactions see Murarka in the recommended readings. For an example of dopant segregation during silicide formation see Reference 1.

Liquid-phase growth has also been used in thin film formation. We encountered an example in Chapter 4 – bulk crystal growth by the Czochralski process. Similar methods are available for thin film growth under the general name of liquid-phase epitaxy or LPE. These typically involve passing a seed crystal across the surface of one or more liquids that freeze new material onto the growing seed as in the Czochralski process. One can produce a multilayer structure by shifting from one liquid solution to another as growth proceeds. Although LPE produces good single crystal thin films at much higher rates than the more common vapor phase methods

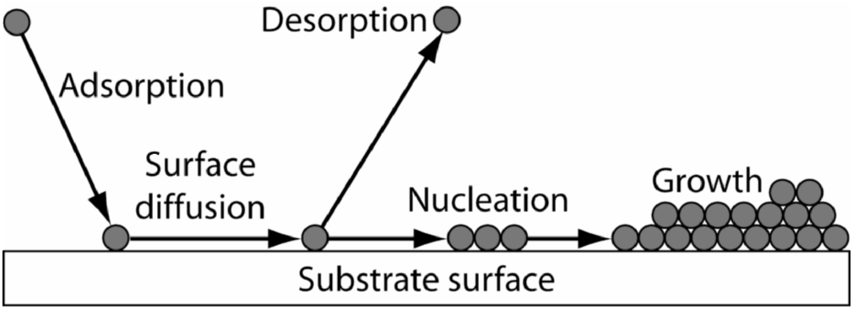


Figure 10.3: Events in a typical vapor-phase thin film growth process.

described below and in the following chapters, the options for control are relatively poor and the temperature is restricted to the melting temperature of the liquid being grown. Thus, it is not possible to grow materials as far from thermodynamic equilibrium, as is possible with vapor phase methods. In LPE, it is also common to remelt some of the substrate when switching from one material to another. This increases the minimum thickness of the layer being grown. Furthermore, remelting is not generally uniform and contaminates the growth liquid. Finally, the temperature is so high in general that diffusion is relatively rapid and abrupt interfaces become difficult to create.

For the above reasons, all of the commonly used thin film growth techniques supply atoms to the growing film from the vapor phase. The major differences among the techniques are the methods used to produce the vapor and the pressure of the chamber in which the growth takes place. In some cases, high-energy particles may also bombard the growing film and cause changes in the growth. The events necessary for film nucleation and growth from the vapor phase are shown schematically in Figure 10.3. Vaporization of species can be by physical or chemical means. Physical vapor deposition (PVD) processes involve evaporation by heat or sputtering by impact of high-energy particles with a target. PVD processes generally produce vapors of atomic or small molecular species. Chemical vapor deposition (CVD) methods use materials that are intrinsically gases under conditions in the reactor and are often supplied through pipes and valves from storage containers. In the following chapters we will consider heat-based vaporization (evaporation) methods, energetic particle based vaporization (sputtering), and CVD separately and in some detail.

Once the vapor has been produced, the steps needed to grow the film are condensation of the vapor on the growing surface (adsorption), surface diffusion of the reactants, reaction to form the film, coalescence of the reacted material into islands of atoms, and desorption (re-evaporation) of any product or unused reactant from the surface. The following sections discuss these steps in more detail.

10.2 GAS PHASE TRANSPORT

Before beginning the description of events on a growing surface, it is useful to consider a few important aspects of the behavior of gases briefly as this is essential to understanding supply of atoms to a surface from the vapor phase, to removal of products in CVD, and to a general understanding of the importance of vacuum conditions.

Gas atoms move at the speed of sound (for given temperature and pressure conditions) and undergo collisions periodically. For gas atoms near room temperature the mean free path λ between scattering events is given roughly by

$$\lambda = \frac{k_B T}{\sqrt{2}\,\sigma P} \qquad 10.1$$

where σ is the collision cross section, typically of the order of 10^{-16} cm^2 and P is the pressure. For T = 300 K and $\sigma \sim 4\text{x}10^{-15}$ cm^2,

$$\lambda = 0.7 \text{ cm } P^{-1} \qquad 10.2$$

where P is the pressure in Pa (1 atmosphere = 1013 mBar = $1.013\text{x}10^5$ Pa). At atmospheric pressure this would yield a mean distance between atomic collisions of ~70 nm. For a typical vacuum system with a source-to-substrate distance of 10-50 cm a pressure of 10^{-2} Pa is sufficient to allow a typical atom or molecule to transit from source to substrate without striking another atom. Higher energy atoms travel, on average, a greater distance. Based in equation 10.1, the distance would increase roughly linearly with kinetic energy. Thus, a 25 eV particle would move ~1000 times farther than a room temperature particle in the same gas.

In addition to mean free path, the flux of atoms striking a surface, or the approximate time between collisions on a particular atomic site on a surface, is important. Ideal gas theory yields a relation between flux and pressure of

$$\boldsymbol{F} = \frac{\boldsymbol{P}}{\sqrt{2\pi \boldsymbol{m} \boldsymbol{k}_B \boldsymbol{T}}}, \qquad 10.3$$

where m is the mass of the gas particle, or

$$F = 2.63\text{x}10^{17} \frac{P}{\sqrt{mT}} \text{ cm}^{-2}\text{ s}^{-1}, \qquad 10.4$$

where the mass is the molecular weight of the gas in AMU, the temperature is in K, and the pressure is in Pa. At 10^{-2} Pa the flux is roughly $3\text{x}10^{16}$ cm^{-2} s^{-1} for room-temperature nitrogen.

When a surface contains a typical atom density of $5\text{x}10^{14}$ atoms cm^{-2} then ~56 atoms strike each site per second at 10^{-2} Pa. Even if only ~2% of them stick to the surface this means the surface will be covered in only one second. For a pressure of 10^{-8} Pa, typical of "ultrahigh" vacuum, the time would be roughly 10^{6} s or about 2 weeks. The significance of this time is that over a space of minutes the surface remains clean to within the detection limit of most analytical techniques. It also means that a film grown at a typical rate of one layer of atoms (a "monolayer") per second (1 ML s^{-1}) will have a maximum contamination due to the residual gas in the vacuum system of one part per million. Doing scanning tunneling microscopy (STM) sets a different standard in surface cleanliness as a single STM image may show one million atom sites on a surface. Hence, a visible contaminant may appear on the surface for every second the surface sits in the vacuum system at 10^{-8} Pa. Therefore, it is common to observe surface contamination by STM and very high quality vacuum is required for this analysis method. What saves most sensitive surface chemistry measurements is the fact that the average residual gas molecule that strikes a surface in ultrahigh vacuum does not stick. After all, if they stuck well they would be relatively easy to pump by creating a clean metal surface. This does work and is used in titanium sublimation pumps, but even when a surface is designed for pumping the sticking coefficient is very small. The process of atoms sticking to a surface is described in the following sections.

10.3 ADSORPTION

The first event in film growth, as suggested by Figure 10.3, is getting atoms or molecules needed for the film to adhere to the surface of the growing material and is known as "adsorption". The essential step in this event is to reduce the energy of the adsorbing species on the surface to below its energy in the vapor phase, preventing its escape. Typically, this happens in a series of stages.

Atoms in the gas phase have a kinetic energy of approximately k_BT where the temperature is that of the vapor source, if little scattering occurs in the gas phase, or is the temperature of the gas if scattering is common. If gas species experience an attractive interaction with the surface (bonding) they accelerate under the attractive force and gain kinetic energy. This is usually much greater than the gas phase kinetic energy. Without some other atom to transfer energy to and without an efficient process for making the transfer, the arriving atom would simply bounce off the surface most of the time, slowing as it returns to the gas but not stopping. This is why reactions cannot normally occur between pairs of atoms in the gas phase. Only when a third particle is present to take away the excess energy is a reaction possible without a reverse reaction being obligatory. In adsorption on a surface the process is much simpler as the surface itself is a reservoir of energy (in the form of heat) and momentum. The arriving particle may exchange these conserved quantities with the surface. Unfortunately, for crystal growth, this exchange does not generally come easily, even in the best of cases.

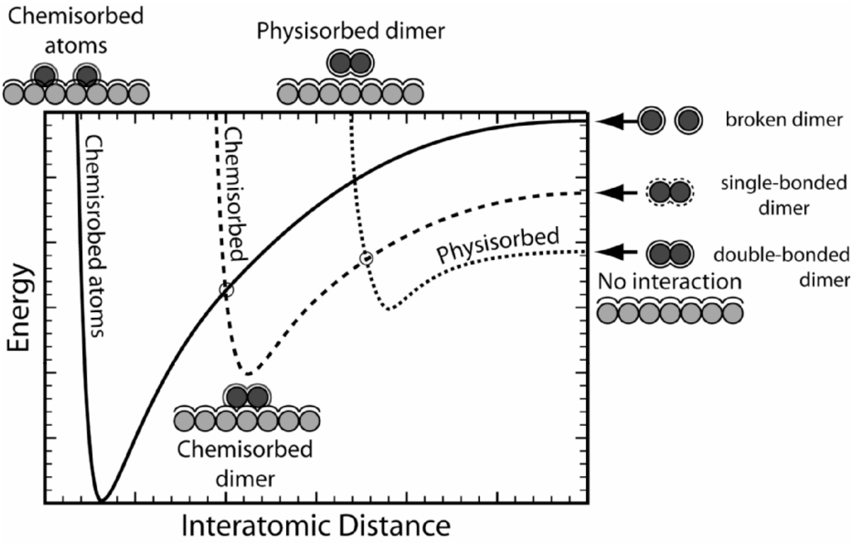


Figure 10.4: Shows an energy-distance diagram for several configurations of a molecule with a surface. Not all of these paths will occur for any given process of adsorption with a surface. In this example the molecule may make transitions from one of the various curves to another as reactions with the surface occur. The lowest-energy transitions are marked with open circles. For an example of a situation where chemisorption is very rare, consider how this figure would appear without the center of the three curves. In that case, transfer from the physisorbed to the chemisorbed case would add much more energy to the adsorbate than would be necessary to induce desorption.

For illustration, let us think of the problem of a diatomic molecule interacting with and adsorbing on a metal surface. The energy of this hypothetical dimer molecule as a function of distance from a surface is shown schematically in Figure 10.4. In the figure the curve with short dashes suggests to the energy-distance relationship for the dimer with unchanged bonding. Thus, if the dimer were O_2 it might be for the case where the dimer has a double bond. The dimer atoms may interact weakly with the surface, but no unpaired electrons are available to form a strong bond. Although both would like to react, the two oxygen atoms are strongly bound to each other and may not spontaneously reorganize their electrons to form a bond to the surface. The result is a van der Waals bond.

Once the molecule is weakly adsorbed it may acquire enough heat to escape back to the vapor (desorb) or it may be able to reorganize its electrons sufficiently to form stronger bonds to the surface. In Figure 10.4, two different reorganizations are hypothesized. These might, for example, correspond to a weaker and a stronger chemical bond to the surface. Each possible arrangement of atoms has its own energy vs. position curve. At a given position along a curve the molecule may be thermally excited such that it changes its orientation and bonding structure to conform to another curve, often with higher energy at that position. It is then free to relax along this curve to the minimum energy position. Such transitions can occur any time a molecule/atom is following a curve with a higher energy than another curve. Note that if one has a dimer initially, and the stronger bonds to the surface require breaking the bonds between the atoms, the energy of the molecule if it desorbed in this state would be higher than in the original gas phase (see Figure 10.4). This may reduce the chances of desorption from the more strongly bound configuration.

A critical issue is the energy necessary to make a transition from one curve to another. If that energy is higher than the energy binding the molecule to the surface in its initial state, then desorption (re-evaporation) is more likely than that it will become more strongly bound to the surface. For example, if the curve crossing points marked with open circles on Figure 10.4 lie above the energy in the vapor phase of the adsorbate in its current bonding configuration, then desorption is likely.

Additional transformations may be required before a molecule reaches its most stable bonding arrangement on the surface. For example, it may be necessary to break surface bonds as well as bonds in the initial gas molecule. Any of these may contribute to any of the energy barriers to adsorption. Therefore, there is generally a good chance that molecules will leave the surface rather than forming a more stable bond. A notable exception to this argument is single metal atoms landing on a metal surface. In this case, both atom and surface have unpaired electrons that can easily interact both to produce a bond and to dissipate the energy of adsorption. Therefore, metals adsorb strongly on metallic surfaces.

For a growth process where a given flux of atoms is arriving at a surface, as described by Equation 10.3, the flux of gas actually adsorbed, Γ, is simply this flux, F, multiplied by the probability, ϕ, for accommodation of the heat and momentum of adsorption.

$$\Gamma = \boldsymbol{F}\phi \qquad 10.5$$

Note that ϕ is typically dependent upon the local chemistry and structure of the surface where the atom is attempting to adsorb. This is relatively constant for a given gas and a given surface. However, as adsorption continues the surface becomes covered with the adsorbate and the adsorption probability may change dramatically. The flux has not changed, only the chance of actually adsorbing. This is usually a consequence of a change in the energy-position relationships.

10.4 DESORPTION

To allow a thin film to grow it is necessary that the atoms not re-evaporate into the gas. Furthermore, in chemical vapor deposition processes some species must evaporate to continue the reaction. Therefore, it is important to also consider the process of desorption. At its simplest, desorption is simply the reverse of adsorption and may follow the same energy distance curve. For desorption of a single atom this simply requires the surface heat and momentum reservoir to supply enough kinetic energy in the correct direction that the atom may escape into the gas. In general the rate per unit area of this process will depend upon the areal concentration of atoms on the surface that are attempting to desorb, an attempt rate constant, and a Boltzman factor. The result looks very similar to a general reaction rate equation:

$$r_{des} = [A]^n \; \nu \, e^{-Q_{des}/k_B T}, \qquad 10.6$$

where [A] is the concentration of desorbing species on a surface, n is the order of the desorption process, ν is the attempt frequency, and Q_{des} is the heat of desorption (usually the same energy that was dissipated in the reverse process of adsorption). For a single atom desorbing into the gas n=1 while desorption as clusters of atoms generally produce larger values of n.

In many cases, the simple desorption of an atom into the gas is a relatively high energy, and hence relatively rare event. Figure 10.3 shows that the energy barrier may be reduced if two or more atoms associate into a dimer or small cluster before desorbing. This is because their energy in the gas phase is lower. The process is known as associative desorption. What is important about associative as compared to simple desorption is that its rate depends, via the law of mass action, on the square of the concentration of desorbing atoms on the surface (n=2) for a dimer desorption or n>2 for larger desorbing clusters. When this concentration is high, desorption is rapid. However, when the concentration is low associative desorption slows considerably. The desorption process is shown schematically in Figure 10.5.

The concentration dependence of associative desorption and the microscopic dynamics of that association forms the basis for operation of devices known as “cracking” sources. These are used to reduce the size of evaporant species leaving a gas source. For example, arsenic evaporates from its own solid as As_4 tetramer molecules. However, from most other surfaces it leaves as As_2. This is simply a consequence of the As concentration, which is high on the bulk arsenic solid and lower on other surfaces even when they contain most of an atomic layer of arsenic. Hence, the dependence of desorption rate on the fourth power of As concentration is not an issue on the bulk solid but prevents this form of desorption on other surfaces. Therefore, adsorbing As_4 clusters from a bulk arsenic source on a surface and allowing them to desorb back into the gas converts As_4 to As_2 (it “cracks” the As_4 clusters). Application of the cracking process to growth by evaporation is discussed in more detail in Chapter 11.

Most group V and VI elements desorb from their own solids as clusters of two or more atoms. In many cases clusters of up to eight atoms may be the dominant desorbing species. However, nearly all of these if adsorbed on another material such as graphite will desorb as dimers.

As discussed above, the desorption process often has a very different rate on different surfaces. For example, if we cool a Si surface and evaporate As onto it we may deposit a thick layer. Upon heating we can desorb this As which shows two distinct desorption behaviors, one associated with As desorption from on top of other As atoms and one for desorption from on top of Si atoms. A detailed example of how H desorbs from Si and how the surface coverages and energies binding the atoms to the surface is presented in the applications section at the end of this chapter.

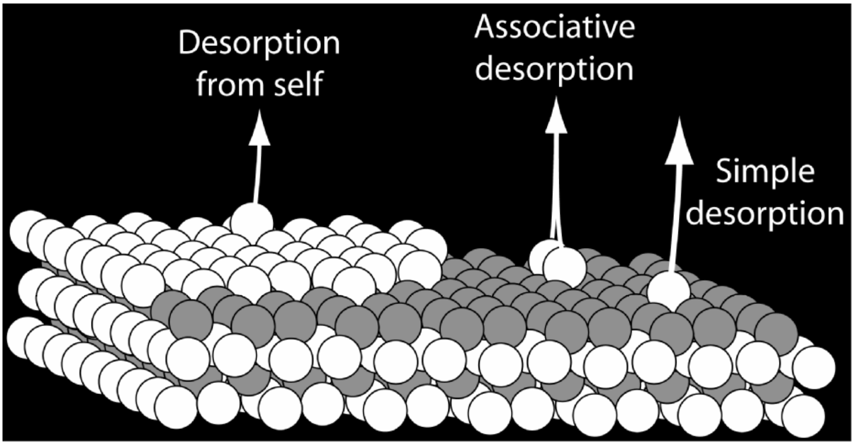


Figure 10.5: A schematic of several desorption processes discussed in the text.

In some cases a reactive site is needed to initiate desorption. For example, the native oxide on GaAs wafers, typically a gallium oxide, desorbs very abruptly. After considerable study it has been shown that the oxide desorption requires a nucleation step creating holes in the layer. These then expand rapidly as the desorption occurs. The desorption reaction can be nucleated by adsorption of a variety of species on the surface. The desorption temperature also depends somewhat on how the oxide is formed and its thickness. When desorption is nucleation-limited there may be a considerable delay in its onset if it is not significantly superheated.

10.5 STICKING COEFFICIENT & SURFACE COVERAGE

Typically during a growth process one has both adsorption and desorption of at least one species going on continuously. When this happens, conservation of atoms indicates that the system must come to a steady-state involving either a balance of adsorption and desorption without net growth of the film; or, if adsorption is faster than desorption, to net growth of the film. The remaining option, that desorption is faster than adsorption means net loss of adsorbate from the surface (the film will evaporate). Because desorption rate depends upon surface coverage, the desorption rate will fall as the surface loses material until it balances the adsorption rate or until the surface is clean.

To determine the surface coverage at steady state we balance the adsorption rate with the desorption rate. Setting equations 10.5 and 10.6 equal:

$$R\phi = \theta^n \ \nu \, e^{-Q_{des}/k_B T}, \qquad 10.7$$

where we have replaced the areal concentration of adsorbate [A] with the unitless fractional surface coverage $\theta = [A]/N_{surf}$ and N_{surf} is the number of surface sites per unit area. The flux F was also replaced with the average arrival rate (in units of inverse seconds) per site, $R=F/N_{surf}$. This puts the equation in area-independent units and eliminates unit difficulties when $n\neq1$. Note that ϕ depends upon the chemistry and structure of the surface on which adsorption is occurring. This equation may be solved for θ^n to get the steady-state surface coverage:

$$\theta^n = R \, \phi \, \tau, \qquad 10.8$$

where we have defined

$$\tau^{-1} = \nu \, e^{-Q_{des}/k_B T} \qquad 10.9$$

with τ being the average residence time of an adatom on the surface. Steady-state adsorption and surface coverage is illustrated in Figure 10.6. As with the adsorption probability, τ will vary depending upon the type of site from which the atom is desorbing, resulting from changes in both ν and Q_{des}.

In typical compound semiconductor deposition processes there will be a low-vapor pressure species that sticks well to the growing surface ($\phi\sim1$ everywhere on the surface). This is the case for Ga in growth of GaAs. The other element has a high vapor pressure and adsorbs and desorbs moderately where the surface is covered with low vapor pressure element (e.g. Ga) and adsorbs poorly and desorbs rapidly where the surface is covered by high vapor pressure material (e.g. As). The low-vapor-pressure species determines the growth rate of the film while the high vapor pressure species is supplied in excess. Whatever does not find a low-vapor-pressure atom to react with and stick to desorbs leaving a stoichiometric compound on the surface automatically.

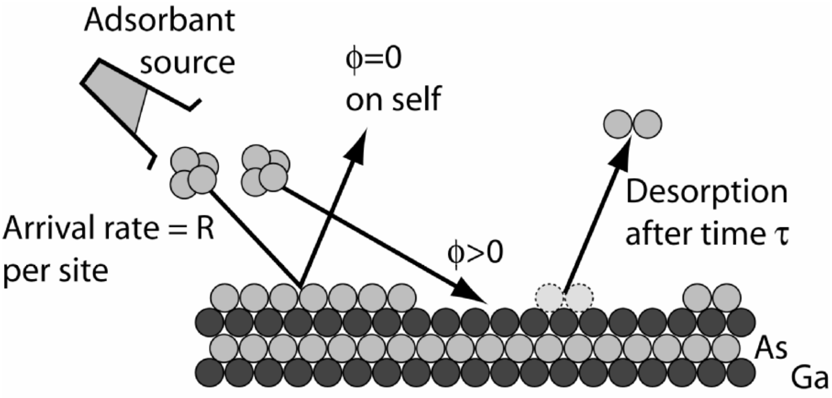


Figure 10.6: A schematic of a simplified version of the balance of adsorption and desorption on a GaAs surface.

Because only a portion of the flux of atoms that arrives at the film surface ends up sticking to and ultimately incorporated into the film, it is common to define the "sticking coefficient" and an "incorporation coefficient" referring to the probability that an atom will stick to and ultimately become part of the film, respectively. The distinction between these two is somewhat subtle. Normally they are the same. However, in a case where an impurity segregates strongly on the surface of the film as growth proceeds, the sticking coefficient may exceed the incorporation coefficient temporarily as the surface segregated layer accumulates, although ultimately at steady state they must match. In segregating species the surface concentration of that species is much greater than the bulk composition within the material. Atoms typically segregate to the surface when they are much larger than the host matrix atoms or when they reduce the surface energy (i.e., they are surfactants). Surface segregation is discussed in more detail in Section 10.7. The incorporation coefficient is generally a sensitive function of surface temperature, fluxes of other atoms arriving at the surface, and steady-state surface coverage for reasons described above. It is therefore a complex quantity and not easily predicted *a-priori*. However, it is the easiest to observe experimentally. One simply measures the bulk concentration of that element and calculates the fraction of the flux arriving at the surface that becomes incorporated into the film.

Because As is supplied as a tetramer when a standard evaporation source is used it has been found to be necessary to look closely at the actual site where the tetramer arrives to determine whether it will stick. One might imagine that an As tetramer would require as many as four open sites on the sample surface sufficiently close to each other to obtain a high sticking coefficient. In practice the number of sites required is closer to two but is significantly greater than one. A theory of sticking of multimeric adsorbates such as As_4 has been developed. For example, Madhukar and Ghaisas referred to the process as "configuration-dependent reactive incorpration" in their model. [2]

10.6 NUCLEATION & GROWTH OF THIN FILMS

Nucleation of a thin film is usually described in terms of classical nucleation theory resulting from coalescence of clusters from a random collection of atoms on a surface. The basic energetics and macroscopic kinetics of nucleation was described in some detail in Section 4.4.2 and will not be repeated here. However, it is useful to look more closely at the atomic processes that are involved in the phenomena described in Chapter 4.

When atoms are deposited on a film surface they produce what is generally termed a "lattice gas", meaning a low-density collection of free atoms diffusing at random among surface lattice sites, occasionally colliding with one another, and presumably occasionally sticking together. Thus, their behavior resembles a two dimensional gas. Single atoms generally move much faster than larger clusters. Therefore, atoms that are bound together are not part of the surface lattice gas. The density of the gas depends upon the rate at which atoms are supplied from the vapor phase by adsorption, lost by desorption, lost by incorporation into atom clusters or islands, or supplied by release from these clusters. In Figure 10.3 the surface atoms on the left side of the figure are part of the lattice gas.

Atoms in the lattice gas interact with others during their diffusion process by moving into adjacent surface sites. From such sites they may continue to diffuse but not into the occupied site of the other atom. Typically, when the atoms are in adjacent sites they are bound together somewhat to form a surface dimer. If while this state lasts another atom joins the dimer the cluster becomes a trimer, and so on. The process is shown schematically in Figure 10.7.

The probability of two atoms joining to form a dimer depends upon the square of the density of single atoms on the surface (n_1) and a Boltzman-type rate constant describing the probability of the atoms sticking together k_{12}. The rate constant incorporates both an effective surface diffusion rate for the moving species and a probability that the particles stick together. Both are temperature dependent. The chance of forming a trimer depends upon the product of a rate constant k_{23}, the density of dimers (n_2) and n_1. Similar terms can be written for higher order events. The backward reaction describing decomposition of dimers into monomers depends only upon the product of the decomposition rate constant and the dimer concentration, k_{21} and n_2, respectively. Decomposition of larger clusters depends upon the concentration of that cluster and a rate constant. A set of differential equations may then be written for the change in concentration with time of clusters of a given size, i, with the general form for a typical island of:

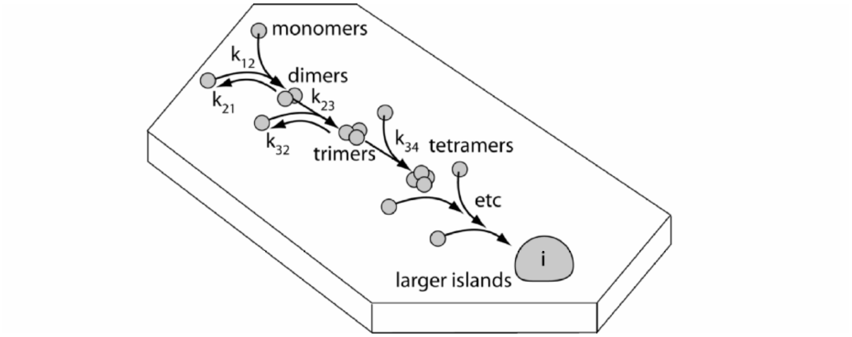


Figure 10.7: A schematic of the process of adatom agglomeration to form small and eventually large clusters.

$$\frac{dn_i}{dt} = \sum_{0<j<i-j} k_{j,i} n_j n_{i-j} - \sum_{0<m<i} k_{i,i-m} n_i + \sum_{\ell>i} k_{\ell,i} n_\ell \,. \qquad 10.10$$

The first term on the right describes coalescence of clusters of size j with those of size i-j. The second term describes decomposition of clusters of size i to sizes i-m and m. The third term represents formation of clusters of size i by break-up of larger clusters of size l. It is also necessary to add terms to account for deposition of atoms or molecules (for example, $F\phi_1$ as in Equation 10.5 added to the equation for n_1, for desorption (by subtracting a term such as $k_{des}(i)n_i$ from each equation), and by the addition of other terms such as may be necessary for a given situation. Note that the chance of sticking to the surface, ϕ, may be dependent upon the surface to which sticking occurs. Reminder: a species may stick very poorly to a surface covered by itself, as is the case for As sticking to GaAs at high temperatures, or may stick very poorly to a substrate other than itself, as is the case of CdS islands on a clean glass substrate where CdS sticks well only to existing CdS islands and not to the clean glass areas.

In practice, decompositions for m>2 (loss of more than one or two atoms at a time) are unlikely unless an energetic particle hits the cluster and breaks it up. Cluster aggregation where j>1 becomes increasingly important when the surface becomes heavily covered by clusters leaving little free space for the lattice gas, as discussed below. Actions involving monomers are generally by far the fastest and hence have the greatest values of k.

To complete the analysis of the equations one requires an estimate of the magnitude of the rate constants k. This estimate, carried out in detail, is complex and beyond the scope of this text. However, several observations on the nature of some of the contributing terms seems reasonable. First, the rate constants include a Boltzmann-like term based on the free energy change, $\Delta G_{j,i}$, for the system upon attaching/detaching an atom to a cluster or for merging two larger clusters. The energy change may be either endothermic or exothermic. This is multiplied by an “attempt frequency” which is related to the diffusivity of the moving species (usually the smaller of the two atoms, molecules or clusters involved in a given event). This attempt frequency also includes a Boltzmann-factor temperature dependence. Thus, the rate constants might be expected to have a general form such as

$$k_{j,i} = D_0 e^{-E_D/k_B T} \, e^{-\Delta G_{j,i}/k_B T} \qquad 10.11$$

where E_D is a diffusion activation energy and D_0 is the diffusion prefactor and could include other constants. The ΔG terms include, among other contributions, an energy such as that described by Equation 4.17 (Section 4.4.2), which is to say by the shape of the total energy curve as a function of cluster size in Figure 4.13. When clusters are well beyond the critical size there is almost no barrier to adding an atom and the diffusion term dominates the behavior, especially when coalescence of larger clusters is considered.

Equation 10.10 represents a potentially infinite set of equations (one for each value of i) in i unknowns. Therefore, the set can be solved for each value of n_i given a starting condition and all relevant rate constants. Such solutions have been carried out many times in the literature.

Because the rate constants are greatest for terms involving movement of monomers (single adsorbed atoms or “adatoms” on the surface), processes involving adatoms are generally the most important. This is particularly true initially, as no clusters exist. Since the first step depends quadratically on n_1, dimer formation is very sensitive to adatom density. Consequently, formation of dimers grows very rapidly. However, when the dimer formation rate constant is low, for example where adatoms do not stick to one another well, and where the decomposition rate is high, formation of dimers and consequently all larger clusters is slow. In this case nucleation is slow and requires accumulation of very high densities of adatoms (which also encourages desorption). When atatoms stick together well and dimers do not decompose rapidly, nucleation is fast and requires low adatom densities. If adatoms do not stick well to the substrate or if single adatoms desorb much more rapidly than atoms desorb directly from clusters, it may be difficult to accumulate enough adatoms to form an initial nucleus. This leads to a delay in nucleation. If one plots the thickness of a film as a function of time in such a situation and extrapolates to zero thickness, one finds that the extrapolation does not lead to zero time. Rather there is a nucleation delay before growth can begin as shown in Figure 10.8.

A rough estimate of the relative rates at which adatoms attach to and detach from clusters may be made by observing that both rate constants will include a Boltzmann term related to the binding energy of an adatom to the cluster. When the binding energy is high (relative to k_BT) the attachment rate constant will be much greater than the detachment rate. When low, the two rates will be more nearly similar. When

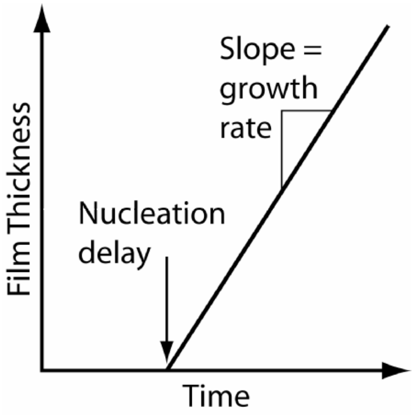


Figure 10.8: A schematic plot of film thickness as a function of time after exposing a substrate to a flux of film material. The plot extrapolates to the nucleation time. Note that this behavior requires desorption of adatoms during the nucleation delay. Otherwise, once nucleation begins all of the atoms deposited earlier would be available to contribute to the thickness.

binding is unfavorable, the dimer formation rate is low. Measurements of film morphologies in the very early stages of growth before islands coalesce as a function of temperature can provide a quantitative measure of the various energies through modeling, for example using Equation 10.10.

An example of the final microstructure of a real surface after the clusters have grown large is shown in Figure 10.9. It is hopefully clear from the figure that the clusters eventually come to occupy a large fraction of the surface. At some point any atom that adsorbs on the surface will meet and stick to a cluster before it sticks to another adatom. This turns off the nucleation process as no new dimers form and the pipeline of small clusters growing into larger ones that constitute the nucleation process is ended.

The end of nucleation actually begins as soon as stable nuclei develop because within some distance of any stable nucleus adatoms tend to be captured by that nucleus in preference to forming new dimers. This leads to a “denuded zone” around the cluster where new clusters are unlikely to form (see Figure 10.10 for a schematic and Figure 10.9 for an example). The greater the diffusion distance for adatoms, the larger the denuded zone around a cluster and the faster that cluster will grow. The most likely area for a new cluster to form is outside of the existing denuded zones. However, as these areas shrink the adatom density in them also decreases and nucleation there also becomes less likely. The formation of denuded zones and the preference for nucleation outside of the existing denuded zones is responsible for the relatively well-organized structure of clusters on the surface.

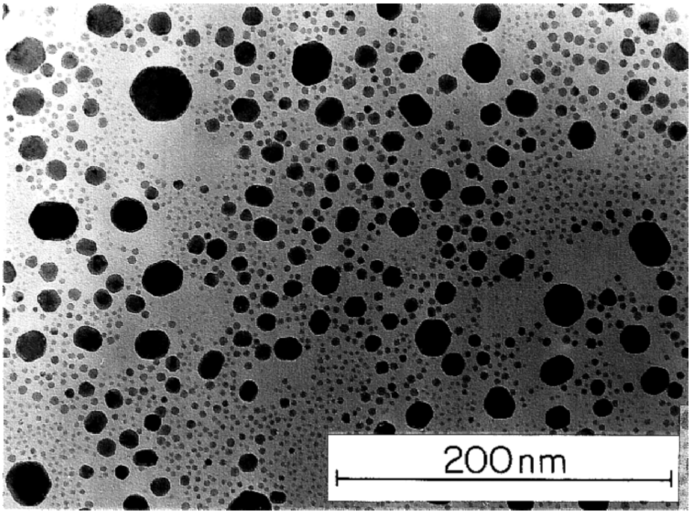


Figure 10.9: An example of a thin In film on an amorphous Si_3N_4 substrate grown by evaporation. See also Reference 3 for experimental details. Used with permission from M.-A. Hasan, S. A. Barnett, J.-E. Sundgren, and J. E. Greene, Journal of Vacuum Science & Technology A, 5, 1883 (1987). Copyright 1987, AVS The Science & Technology Society.

Even clusters that are very large and very stable (as indicated by Figure 4.13 and Equation 4.17) will lose atoms, $k_{i,i-1} \neq 0$. Although the most likely fate for these atoms is to reattach to the cluster that they left, inevitably some manage to escape and either form new nuclei or become attached to another cluster. This leads to a gradual process of exchange of atoms among clusters. The process can be rapid or slow in absolute terms or relative to the growth rate of the film. If it is rapid, with or without net growth, the clusters with the greatest stability gain atoms at the expense of the clusters with the lowest stability. This is because their adatom attachment rate relative to the detachment rate is larger than for less stable clusters. Thus, the small clusters, which are usually less stable, gradually disappear and the larger, more stable clusters grow. The exchange of atoms leading to growth of large clusters and shrinkage of small clusters is known as coarsening.

The process of coarsening is helped along if even relatively large clusters can move on the surface and hence can coalesce with one another. This movement is observed experimentally at sufficiently high temperatures. Cluster diffusion results from the fact that atoms may move around the perimeter of the cluster as well as leaving it to join the lattice gas. This results in random transport of atoms from one side of the cluster to the other and hence to movement of its center of mass. The larger the

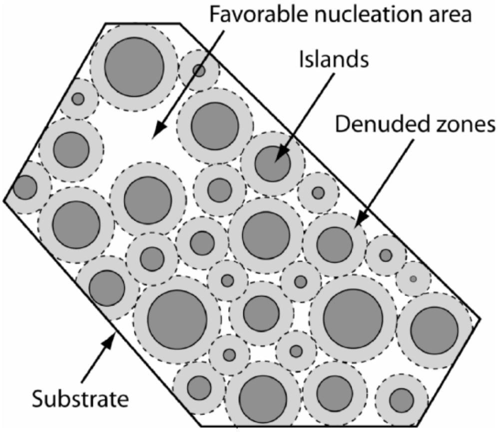


Figure 10.10: A schematic of the effect of capture of adatoms by large islands on nucleation. The denuded zones are areas relatively free of adatoms where further nucleation is unlikely. The white areas between the denuded zones may show nucleation, although the smaller these areas, the fewer adatoms are present on average, the less likely is nucleation, and the slower is growth of any island that does form.

cluster the more atoms must move in order for it to shift its position. Hence, larger clusters diffuse much more slowly than smaller ones. When two clusters touch they usually rapidly shift to an equilibrium shape (hemispherical or faceted in most cases) through movement of atoms around their perimeters.

As the clusters grow they may also coalesce without diffusion by simply coming into contact. Again, this is usually quickly followed by clusters reshaping themselves by diffusion across their surfaces. Coalescence eventually leads to complete coverage of the substrate with the growing layer. At this point there is a motivation to flatten the surface as much as entropy, atomic transport and surface energy differences from one plane of atoms to another permit. The smoother the surface, the less its area. Since the surface energy is always unfavorable, minimizing surface area is preferred. Ideally, the surface would be atomically smooth. However, entropy at finite temperatures prevents this from happening.

The result, near to an ideal overall orientation, is a surface consisting of relatively smooth terraces, occasional high points (clusters of adatoms), and various smaller structures including free adatoms. Any real surface will include surface steps that have a much larger radius of curvature than any other feature. As with surface islands on a foreign substrate, atoms may be transferred from small clusters to larger ones on a smooth surface. Ultimately they prefer to transfer to a surface step. This exchange process is shown schematically in Figure 10.11 and is the basic process of surface growth after coalescence of the film. If one stops growth and allows the surface to anneal, islands will typically disappear as atoms transfer to the (most stable) surface steps.

10.7 SURFACE DIFFUSION

Because growth mechanisms for thin films are so strongly determined by how atoms are transported across the surface, it is appropriate to pause to consider diffusion of atoms at the atomic scale in more detail.

Atoms on surfaces will always have preferred locations locally relative to underlying atoms. Sometimes this will be on a dangling bond, sometimes on top of an atom, and usually in a "hollow" between atoms. The preferred location is determined by the electronic structure of the surface and the possible bonding configurations. One can calculate the energy of various configurations of atoms on a surface, as shown, for example on the Si (001) 2x1 surface near a step edge, in Figure 10.12. This figure shows a map of the energy of a solid, calculated with a density-functional theory computer code [4] with an adatom placed at various locations across the surface. Different calculation methods may obtain different energy maps. However, the results illustrate the important phenomena involved in atom transport on a surface. The Si (001) 2x1 surface consists of rows of pairs of atoms (dimers) on top of a square grid of atoms below, as shown in Figure 10.12 (c). The dimers form because each atom on this surface has two dangling bonds sticking into the vacuum on opposite sides of the top atoms.

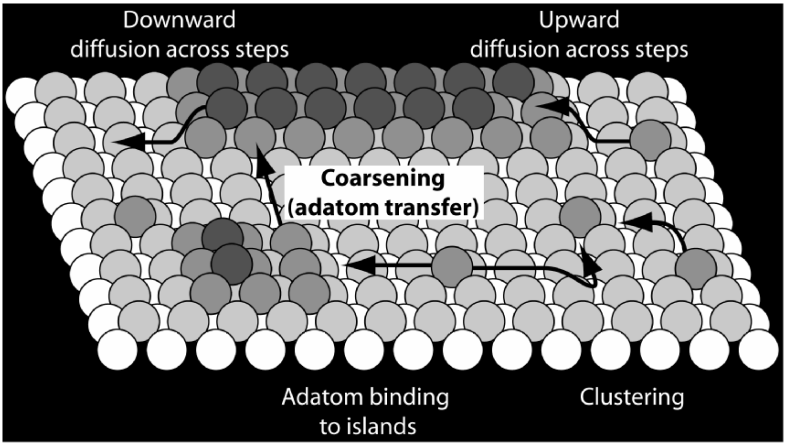


Figure 10.11: A schematic diagram showing typical routes of transfer of adatoms across a growing crystal surface among islands, between islands and surface steps, and across the steps.

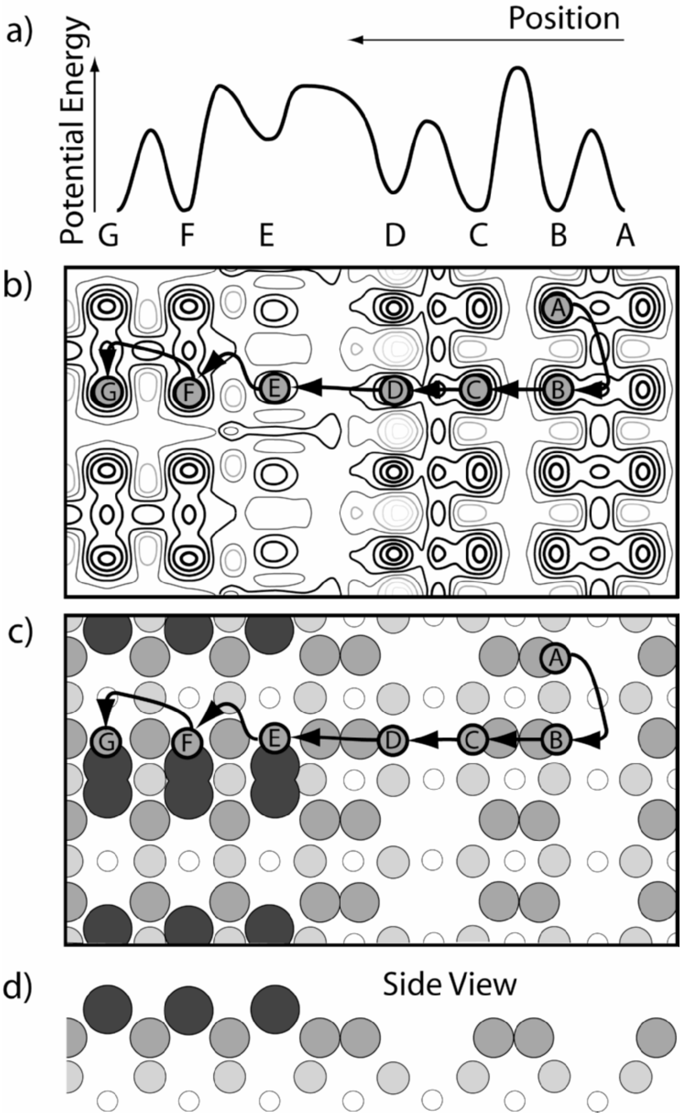


Figure 10.12: A schematic figure for atomic diffusion across a surface step on a Si (001) 2x1 surface. The approximate energy contour for the atom (a) following the path on the surface shown in the middle two portions of the figure is at the top. Regions of strongest binding of an adatom to the surface are shown with darker contours. A side view of the surface step (d) and a top view (c) as well as the full energy surface contour map (b) around the step edge are also given. (After results in Wang, Drabold and Rockett [4].)

By rocking the atoms on the surface toward one another bending the bonds connecting the top atom layer to the second layer, pairs of these dangling bonds may join to form new bonds. Thus the atoms on the surface, rather than having two dangling bonds each, have only one at the cost of distorting their bonds to the layer below. The dangling bond orientation in the surface plane rotates by 90° with the addition of a new layer of atoms. Thus, the rows of dimers also rotate with each step. This results in two types of surface step, one with the dimer rows on the upper terrace running parallel to the step edge, and one running perpendicular. The example shown in Figure 10.12 includes the latter type of step. When an atom diffuses on such a surface, its energy changes as it moves from one ideal site to another. Generally, on the energy landscape there will be maxima, minima, and saddle points. The atoms will typically reside at the minima and will move from site to site via saddle points as suggested by Figure 10.12.

One can see from the surface potential map [Figure 10.12 (b)] that [this simulation concludes that] the Si adatom prefers to bind to the dangling bond of one of the atoms in a dimer and moves along the dimer row through the channel between dimers from one dangling bond to the next. It is easy to switch from one side of the inter-dimer-row channel to the other. The hard step is to cross a dimer row from the dangling bond on one side of a dimer to the dangling bond on the other side. Thus, diffusion on this surface is highly anisotropic. Adatoms move rapidly along the dimer rows but only slowly across the rows. This has consequences for the resulting surface structure and growth. Islands of atoms that form are highly anisotropic.

When an atom encounters a surface step it is entirely possible that there will be a significant energy binding it to the step edge, repelling it from that step, or preventing it from crossing the step edge. The barrier to crossing the step may resist either upward or downward crossing of the step or both. The presence of a barrier to crossing steps, known as a “Schoebel-Ehrlich” barrier after the seminal works by groups led by these two scientists, [5,6] results in formation of new islands of atoms at step edges, surface roughening, and asymmetric growth. The example shown in Figure 10.12 indicates that the step is mildly repulsive to single adatoms. The binding energies at sites D and E along the step edge are higher than at sites on the upper or lower terraces (A, B, C, F, and G). Furthermore, the energy necessary to move from site F to site E is considerably higher than to move from F to G. Consequently, an adatom is most likely to return to the upper terrace from position F than to reach the step edge. Likewise, an atom approaching the step from below finds site D less attractive than site C and the energy barrier higher to move from site D to E, climbing the step edge.

The consequence of these predictions is that single adatoms will tend to stay away from this type of surface step and growth will not occur there until the dimer bound to the lower step edge is broken. The repulsion of adatoms by the step would also enhance nucleation of new adatom islands in the surrounding region because they have two directions to move on the open terrace but only one near the step. This results in a lower effective diffusivity and a higher adatom density around the step edge. The behaviors outlined here would normally result in a very rough growth surface. However, in the case of Si, the adatoms meet each other and form dimers on the open surface. It turns out that the dimers are themselves mobile and are the primary diffusing species participating in film growth. They move relatively isotropically and are less influenced by step edges. Still, the slow growth rate of the step shown in Figure 10.12 and the fast growth rate of the other step orientation leads to characteristic surface morphologies on the Si (100) surface.

The details of the dimer behavior are much less known than for single adatoms because it is difficult to do detailed *ab-initio* calculations similar to those above for a moving dimer. There are too many cooperative modes in which movement can take place. [*Ab-initio* means that the calculation does not rely on experimental data and the result is not a "fit". Rather, it is calculated from fundamental physics such as was outlined in Chapter 5. Indeed, the density functional *ab-initio* method used for Figure 10.12 is based on the LCAO approach.] The calculations are very time consuming for more than a few hundred atoms and so only a few configurations can be examined.

10.8 SURFACE ENERGY

Much of the surface structure observed in thin films grown from the vapor phase may be attributed to the surface energy of the material or the substrate or the energy of the interface between the two. Therefore, a discussion of surface energies is valuable to understanding thin film growth. Surface energy is highly dependent upon the number of dangling bonds on a surface and whether electrons in these dangling bonds are paired with others, whether the dangling bond is empty, or if the surface includes unpaired electrons. Unpaired electrons raise the surface energy significantly in covalently bonded materials.

As an example, consider the case of Si discussed above with reference to surface diffusion. The three common surface orientations for which it is most easy to purchase polished substrates are the "low-index" (100), (110), and (111) surface planes. The Si (100) surfaces in two structures (with and without surface reorganization ["reconstruction"] to reduce the number of dangling bonds) are compared to the unreconstructed Si (111) surface in Figure 10.13. Note that the simple, unreconstructed Si (100) 1x1 surface has two dangling bonds per atom, each half filled with electrons. The reconstructed Si (100) 2x1 surface has one dangling bond per atom but some of the surface bonds are distorted. Finally the stable unreconstructed Si (111) 1x1 surface has one dangling bond per atom, each half filled. Even the cases shown in Figure 10.13 are simplified because the Si (111) surface can undergo a further complex reconstruction to pair the electrons in the dangling bonds. This results in a surface with adatoms lying off proper lattice sites in the top layer in a "dimer-adatom-stacking fault" structure. [7] The Si (100) 2x1 surface includes one undesirable half-filled dangling bond per surface atom. This can

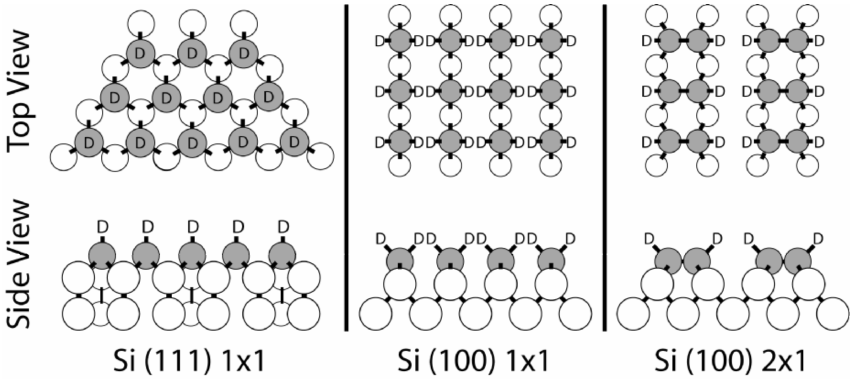


Figure 10.13: Shows the surface structure of three surfaces, the unreconstructed Si (111) and two forms of the Si (100), with and without the typical reconstruction. The (100) 1x1 surface is not observed experimentally because of the large energy gain due to reconstruction. At temperatures below ~700°C the Si (111) surface reconstructs. The "D" labels indicate the position of dangling bonds. On this surface, each is half filled with electrons.

be improved by tilting each dimer and changing the bonding such that one atom in the pair has more electrons in the dangling bond and one has fewer. This partially pairs electrons in one dangling bond while partially emptying the other. The tilt alternates along the dimer row, leading to a 2x4 surface structure (repeating every two lattice spacings in one direction and every four in the other).

The surface energies for the selected Si planes (with relatively low energies), as measured by Eaglesham et al.., [8] are 1.23, 1.36, 1.38, and 1.43 J m^{-2} for the (111), (100), (311), and (110) surface planes, respectively. Given enough atomic mobility during growth, the surface will adopt the lowest energy atomic arrangement. Ideally the surface will consist entirely of the lowest-energy planes. However, where these planes meet it may be better to produce a moderate energy surface plane to connect them. The equilibrium shape of an interior void in a solid will therefore typically consist of a mixture of relatively low-energy planes. Determination of the resulting void shape is by a Wulff construction. This is accomplished as follows (see Figure 10.14 for example). One draws, in three-dimensional space, planes at appropriate angles for their indices at a distance from the plot origin equal to their surface energy. The equilibrium shape of a void or gas bubble in a solid will be the shape of the space contained within all such planes. The construction also has relevance to the equilibrium shape of surface facets on a thin film. Concerning the example shown in Figure 10.14, no {111} or {311} plane lies perpendicular to the (100) and (010) planes simultaneously. Therefore, the planes lie at an angle to the drawing. To be correct, one must project the various planes onto a given surface in which the plot is being made. In the example, this tends to enhance the length of the {111} and {311}

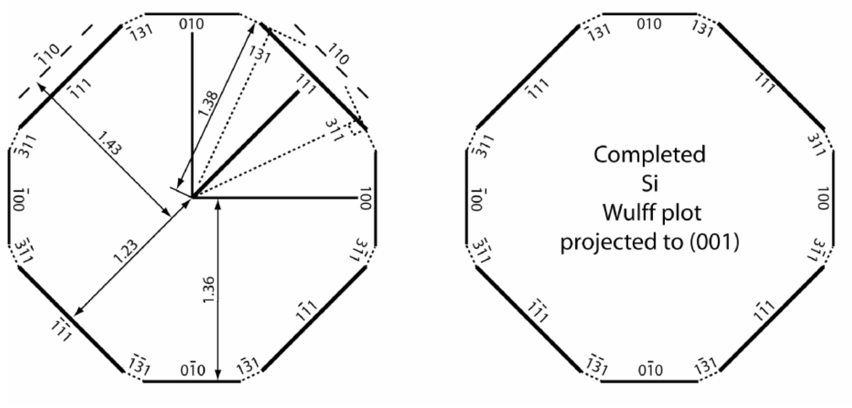


Figure 10.14: Shows the construction of a Wulff plot for Si based on data in Eaglesham, Reference 8. Note that because the four planes indicated do not lie perpendicular to a single plane, the perpendiculars shown in the figure are projected such that they are in the same plane. Therefore, the distances are the projected lengths on the diagram. The shape of the Wulff plot should be approximately correct based on the observed void pubished in Eaglesham et al. [8]

lines relative to the {100} sides. Note also that because the {110} planes have higher energy than the others, they do not form spontaneously in most of the void.

An example of the ability of a semiconductor surface to decompose during growth in an attempt to minimize the surface energy is shown in Figure 10.15 for the chalcogenide semiconductor $CuInSe_2$ grown by an evaporation-like process. [9] Although the average surface orientation for this film is {110}, the film has decomposed into close-packed planes of opposite polarities, equivalent to the {111} planes of Si in general atomic arrangement. A series of studies of the growth of this semiconductor shows such a strong tendency to form these planes, that most surfaces facet strongly to the low-energy orientation. Similar results can be found by examining voids within grains of $CuInSe_2$. Most other semiconductors do not show this strong a preference for one type of surface and a mixture of orientations would be expected both in voids and on free surfaces, as was the case for Si.

The surface energy of a solid can be considerably reduced by accumulation of a foreign atom on the surface. For example, if one considers the Si (001) 2x1 surface in Figure 10.13, if the top layer of Si atoms were replaced with a group V element such as As, an extra electron would be available to each surface atom. This would permit pairing of the electrons in the dangling bond without further reconstruction. Indeed, this is what is observed when Si is exposed to As. A strongly-bound monolayer of As forms on the surface and significantly lowers the surface energy. Any material which lowers the energy of a surface is known as a “surfactant”.

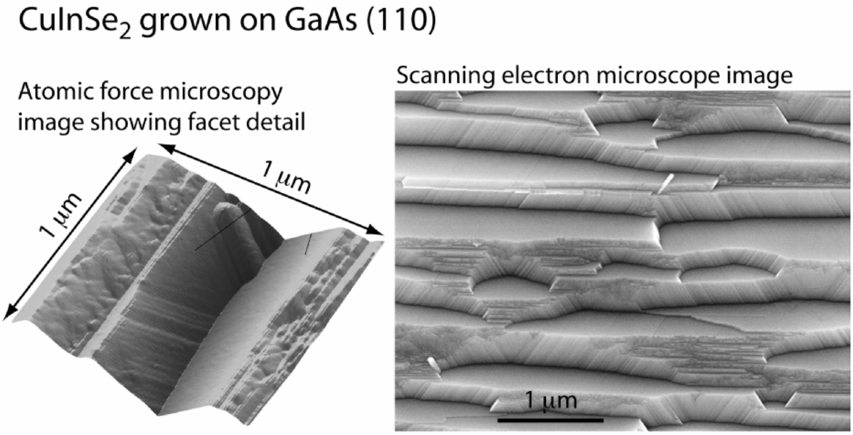


Figure 10.15: The surface of an epitaxial layer of CuInSe$_2$ grown on a (110)-oriented GaAs wafer. The surface has decomposed into two sets of facet planes with close-packed surfaces similar to the (111) in Si and other diamond-structure semiconductors. One of the two facet planes is rough because growth is occurring on that plane and the other is smooth.

Surfactants are problematic as dopants in semiconductors because there is a strong driving force for them to remain on the surface as a film grows, rather than being incorporated into the material. Therefore, the incorporation probability is much lower than the sticking coefficient, at least on an initially clean surface. For example, in Sb doping of Si it is common to observe a surface concentration more than six orders of magnitude greater than the bulk concentration.

In general, a fixed ratio of bulk impurity atom fraction to surface atom fraction is observed at a given temperature. Higher temperatures usually result in more incorporation as entropy favors mixing the atoms on the surface with those in the bulk. As one would expect, the extent of surface segregation decreases exponentially with temperatures when atom mobility is rapid. By contrast, when the impurity has a relatively low mobility, it will tend to be buried by new layers of atoms as they are deposited. This results in more segregation as the temperature increases due to an exponentially increasing diffusion rate with growth temperature. Decreasing segregation with increasing temperature thus indicates an equilibrium segregation ratio, while increasing segregation indicates a kinetically limited segregation process. Both are observed experimentally.

In addition to segregation driven by reduction of surface energies, strain energy can drive atoms to the surface. Thus, large atoms such as Sb in Si are favored on the surface because the surface can relax to accommodate them better than is possible in the bulk. One can calculate the energy of a misfitting spherical inclusion in the bulk of an elastic solid following the procedure of Eshelby. [10] The resulting energy is:

$$E_{elastic} = \frac{8\pi(1+\nu)}{3(1-\nu)} G\, r_{imp}^3\, \varepsilon^2, \qquad 10.12$$

where ν is Poisson's ratio and G is the bulk modulus for the matrix, r_{imp} is the radius of the spherical inclusion, and ε is the strain caused by that inclusion, see Figure 10.16. The strain is assumed to result from cutting a spherical hole out of the solid, inserting the misfitting inclusion into it, and allowing the system to relax. The change in radius of the space containing the inclusion is the strain.

This elastic energy drives segregation as do surface electronic considerations. Therefore, a large atom segregates to the surface of a solid very strongly in general. Small atoms can either segregate to a surface, driven by an ability to reduce surface energy, or may prefer to be in the solid. One may see how a driving force may exist to pull a small atom into a solid from the discussion in Chapter 5. As the lattice shrinks, if the bonding is otherwise relatively unperturbed, the bonding-antibonding interactions strengthen and the energy of the electrons in bonding states is lowered. Perhaps it is not surprising then to learn that B segregates preferentially into rather than out of Si.

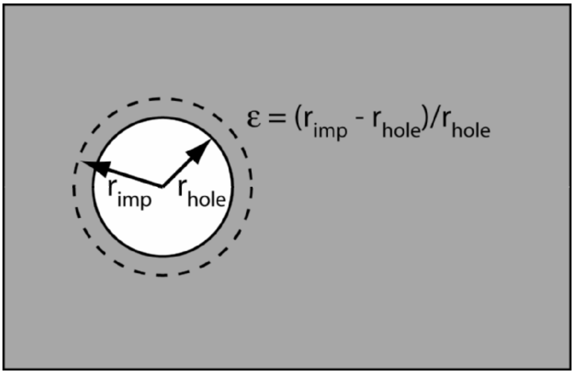


Figure 10.16: A schematic of the geometry of a misfit inclusion in a solid based upon which the strain energy is calculated.

10.9 MORPHOLOGY DETERMINED BY NUCLEATION

In addition to forming surfaces based on equilibrium energy relationships, non-equilibrium shapes may be determined by the process of nucleation and growth of the material. The nucleation process described in Section 10.6 leads to small islands on the surface. With sufficient atomic mobility these may have surface facets approximating the shape of the Wulff plot for that material. However, both the interfacial and surface energies and the surface lattice misfit also determine how the film grows.

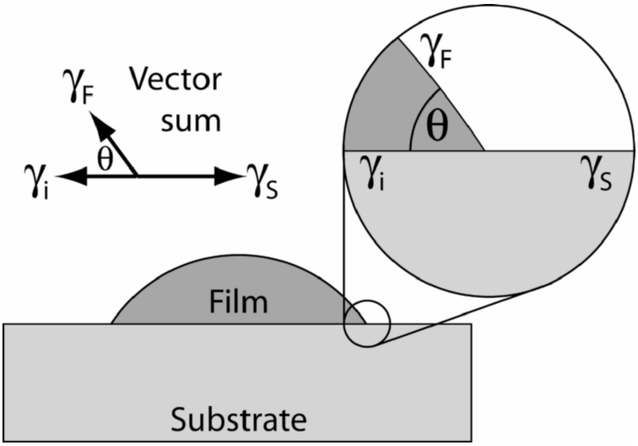


Figure 10.17: The geometry of an island of film on a substrate surface showing the contact angle and relevant energies.

Whenever a film is grown where one layer alternates with another (a superlattice), for example, GaAs layers alternating with (AlGa)As in the distributed Bragg reflector of a VCSEL laser diode (see Section 3.6.2.2), the surface energy must increase with one of the two layers grown, while it must decrease with the other. In the case of the example, GaAs has a lower surface energy for the typical (100) orientation compared to (AlGa)As. When the surface energy increases by replacing substrate surface with film surface, there is a motivation to minimize the amount of substrate covered by the film. In other words, the film will pile up in islands. This is why (Al,Ga)As tends to roughen when grown on GaAs. On the other hand, when the film lowers the surface energy there is a tendency of the film to spread across the surface, completely covering it, as for GaAs on (Al,Ga)As.

The equilibrium shape of a hemispherical island on a surface whose behavior is driven entirely by surface energy considerations will form an angle with the surface known as the contact angle, as illustrated schematically in Figure 10.17. This also applies to liquid droplets on surfaces, where the contact angle is particularly easy to observe. One may calculate this angle from the surface free energy change, ΔG_{surf} resulting from a change in the shape of the island, which changes the contact area, ΔA between the island and the surface:

$$\Delta G_{surf} = \Delta A(\gamma_i - \gamma_S) + \Delta A \gamma_F \cos(\theta - \Delta\theta) \qquad 10.13$$

where γ_i, γ_S and γ_F are the interface energy between the film and substrate and the surface energies of the substrate and film, respectively. The equilibrium condition is given in the limit of small ΔA by:

$$\frac{dG}{dA} = \gamma_i - \gamma_S + \gamma_F \cos(\theta) = 0 \qquad 10.14$$

assuming that in the limit of small ΔA, Δθ is also very small relative to θ. A brief examination of this formula with reference to Figure 10.17 will show that this looks like a force balance (vector sum) of the three surface energies where the film joins the substrate. It is a balance between the energy where the island is (both film surface and interface) and where the island is not (substrate surface). It is from contact angle measurements that much information about surface and interface energies are obtained.

The lattice mismatch between the film and substrate (discussed in detail in Chapter 7) also has an effect. Recall that strain energy increases with increasing thickness and that strain relief occurs when dislocations form at the film/substrate interface. This means that even when a film lowers the surface energy, it may still be energetically unfavorable to grow many layers of a relatively thin film. Rather, once the surface energy is reduced it may be favorable to pile the atoms up to take advantage of either local strain relief where a dislocation did form, or to reduce the strain energy by distortion of the island itself, as in Figure 7.23.

The combination of growth of a monolayer or two to reduce surface energy followed by island formation is referred to as the Stransky-Krastanov growth mode. Growth of islands without the thin layer to reduce surface energy (in the event that the new layer raises the energy) is Volmer-Weber growth, and a two-dimensional layer-by-layer growth mode is called Frank-Van der Merwe growth. The three modes are observed within ranges of strain and surface energy change as illustrated in Figure 10.18. These growth modes have been modeled in detail using molecular dynamics by Grabow and Gilmer with detailed discussion in Reference 11.

Finally, the orientation of the film atomic planes should be noted. When a grain in a thin film can match its lattice to that of the substrate, there is considerable motivation to do so as this greatly reduces the density of dangling bonds. Therefore, it is common to find an influence of a crystalline substrate on the texture (the tendency to develop a non-random average grain orientation) of a growing thin film. The ultimate example of this is epitaxy, where the film is fitted to the lattice of a single crystal substrate across an large area.

The most common observation of all is when the film cannot make any satisfactory alignment with the substrate and therefore effectively ignores it. This is also the case for deposition of a thin film on an amorphous substrate. In such a situation the film typically chooses to put its atoms as close together as possible to maximize bonding among them. This leads to a strong preference for nucleation of grains with a surface

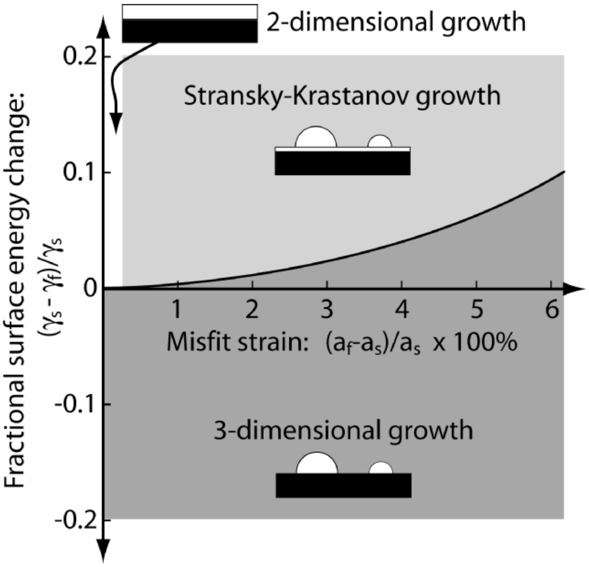


Figure 10.18: Shows the regions of misfit strain and surface energy phase space in which different growth modes are observed. At small misfit strains a film that lowers the energy of the surface produces smooth layer-by-layer growth. When the surface energy is raised by the film or when the strain energy is too large the growth is three-dimensional. As an example, the fractional surface energy change for growth of Si on Ge is +0.1, the misfit strain is 4%, and the growth mode is Stransky-Krastanov. The smooth layer is about three monolayers of Si before the growth switches to formation of islands. Ge growth on Si is by island growth without a smooth covering layer, as one might expect. Figure based on the analysis of Grabow and Gilmer.

that is a close-packed plane. This is why most thin films with a bcc crystal structure tend to show a (110) preferred orientation, while diamond and other fcc crystal structures tend to show a (111) preferred orientation. Note that this is not the reason for faceting of a surface such as was shown in Figure 10.15 as the facet planes, while close-packed, are not parallel to the substrate surface.

10.10 MICROSTRUCTURE EVOLUTION

The structure, morphology, and preferred orientation of a thin film is often very different from that of the nuclei that formed on the substrate surface, especially in the case of polycrystalline films. Before turning to that case, let us consider briefly the relatively simple case of the surface morphology of epitaxial layers. We saw in the previous section that when a film grows epitaxially it may roughen due to either surface energy or interfacial strain effects. However, the surface morphology may evolve significantly after the initial nucleation phase is complete. This may lead to either roughening of a relatively smooth film or to smoothening of a film that nucleated as islands.

A film that forms on a very smooth substrate and lowers the surface energy may grow as a very smooth layer itself. However, at either very high or very low temperatures, roughening may occur. At low temperatures atoms cannot move far enough from their initial adsorption point to reach the lowest point on the surface. Furthermore, if movement across surface steps is difficult then the more steps that form on the surface the shorter distance the adatoms can move. These factors lead to roughening of the surface as time goes on. If one stops growth and allows the surface to anneal, this roughness will gradually heal as atoms have time to assume their lowest energy positions. However, if roughness is allowed to accumulate, defects are often incorporated into the film. These defects increase the chances of further growth errors occurring. The defects may also collect together to produce grain boundaries. Thus, at sufficiently low temperature there will come a point where epitaxy breaks down and the film will become polycrystalline or even amorphous. In general, beginning from a perfect single-crystal surface, growth at a given temperature and rate can go on for a relatively fixed time before the transition to polycrystalline or amorphous material ensues. The result is a relatively well-defined layer of epitaxial material with a thickness known as the “epitaxial thickness” under the amorphous or polycrystalline layer.

Deposition at very high temperatures may also lead to surface roughening because the atomic mobility in the new layer is greater than in the underlying substrate. Now roughening is the result of entropy, which favors a rough surface to increase entropy in contradiction to surface tension that prefers a smooth surface. In some cases roughening can also be the result of a change in surface composition due to high temperature desorption of a species that is stable on the surface at lower temperatures.

10.11 RESIDUAL STRESS AND ADHESION

As a final brief note on thin film growth in general, a technologically important aspect is adhesion of the film to the substrate. Good adhesion normally requires the film to have the lowest possible stress, as any force applied to the interface will encourage decohesion. The most successful adhesives such as epoxy form a stress-free junction. Minimizing stress in a thin film is usually a matter of adjustment of deposition conditions. Two factors contribute to stress in a film, differential thermal expansion and deposition-related processes.

Deposition-related processes are the result of the mechanism of accumulation of the film on the substrate. A simple deposition process producing islands on the surface as in Figure 10.9 and 10.10 inevitably leads to shadowing of portions of the surface from the incoming flux as islands come together. The source of this shadowing is shown schematically in Figure 10.19. When atoms do not move sufficiently after

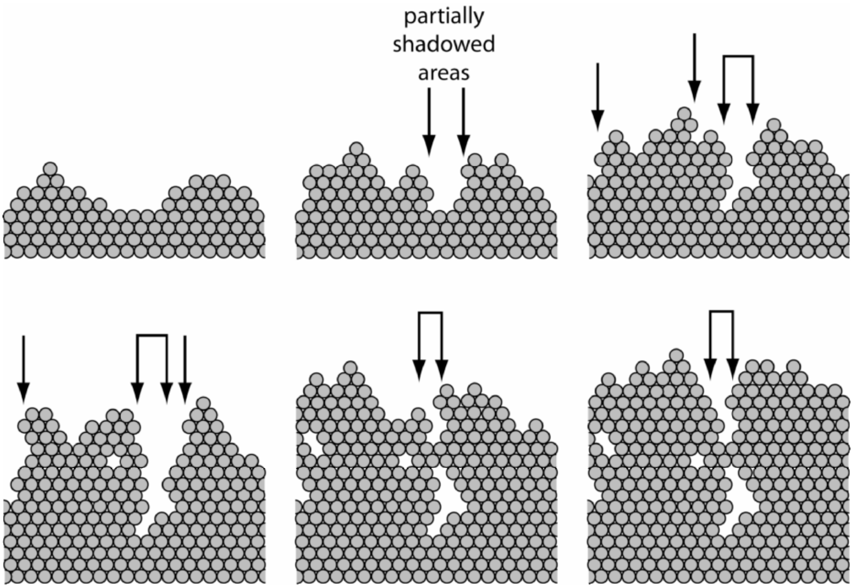


Figure 10.19: A schematic diagram of a thin film growing from a flux of atoms from directly above. Shadowing results from overhangs and protrusions in the growing material and leads to trapped voids in the films and in low-density grain boundaries.

deposition to fill gaps and shadows between coalescing islands, the result is narrow voids between columnar grains in the film, possibly nothing more than a somewhat low-density grain boundary. Because some atoms either make direct contact or form loose long range bonds between these columns, there is a bonding force that attempts to draw the columns together, while bonds to the lower portions of the column and its intrinsic stiffness tends to hold the columns apart. When the flux of atoms is at an angle to the surface these voids are both enlarged and directed toward the source of atoms, if the deposition process provides a flux from a single direction. A film that is moved continuously under a point or line source of atoms this may even cause the columns to wobble from side to side. The result of polycrystalline film growth at low temperatures is a tensile stress in the film that would cause its contraction were it not for the presence of the substrate. This often leads to tensile stresses in the films and possible adhesion failures.

When the film is bombarded during growth with energetic particles, atoms may be knocked into the intergranular voids, filling them even at relatively low temperatures. This knock-on process may drive the film into compressive stress if more atoms are pushed into lower layers of the film than it intends to accommodate in its preferred crystal structure. Thus, the residual stress may be adjusted if a

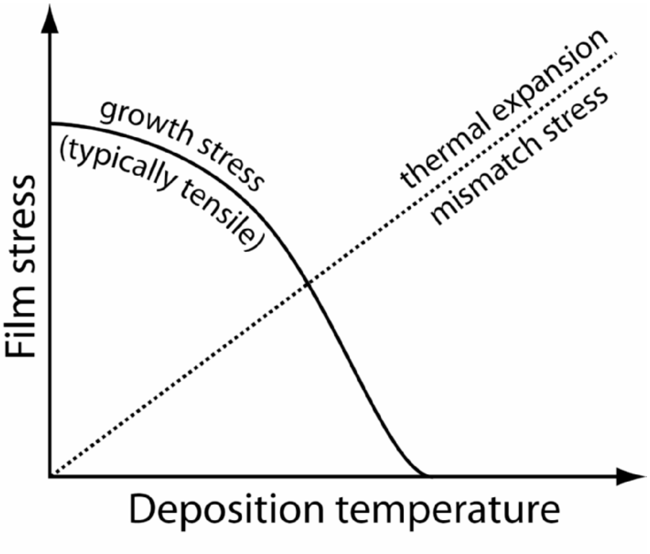


Figure 10.20: The effect of substrate temperature on film stress. Note that the thermal expansion mismatch stress can be either compressive or tensile while the growth stress is generally tensile at low temperatures. If the thermal expansion stress is tensile then the total stress is the sum of the two curves shown. If the thermal expansion stress is compressive then the total stress is the difference of the two curves.

mechanism is available to adjust the amount of energy and flux of particles bombarding the growing film surface (see Chapter 11).

The differential thermal expansion contribution to film stress is straightforward to understand. When a film is deposited it typically has only the growth stresses described above. However, if the deposition temperature is significantly different from room temperature (usually higher) then when heating is terminated after growth and the sample cools, the film usually contracts at a different rate than does the substrate. Because the substrate is usually very much stiffer than the film this differential thermal expansion stress is accumulated in the film.

The net stress in a film is the sum of the growth stress (typically decreased by increasing growth temperature) and the thermal expansion stress (typically increased by increasing growth temperature). The normal behavior is shown schematically in Figure 10.20. High stresses cause adhesion failures. On flexible substrates high stresses also cause curling of the substrate.

In addition to residual stresses, adhesion failures result from a lack of chemical reaction between the film and substrate, which leads to a weak interface; very smooth surfaces, which allows large forces to be projected onto the interface with no mechanical interlocking of the substrate and film; and contamination of the substrate surface. The latter is both most common and most easily dealt with. A combination of cleaning with solvents and ion bombardment of the sample surface prior to deposition can be highly effective in removing contamination. Surfaces are also roughened by ion bombardment, which can enhance adhesion. Finally, mixing the atoms across the interface on the scale of a few tens of atom layers can substantially enhance adhesion.

In production, deposition processes, surface cleaning and careful process control to minimize film stresses and maximize adhesion.

10.12 APPLICATIONS

The discussion in these examples makes significant reference to the growth techniques described in the following chapters as these are the practical implementations of the methods described in this chapter. Therefore, the reader is frequently referred to these chapters for more details.

10.12.1 Adsorption, desorption and binding of H to Si

A simple place to begin with some examples of concepts described in this chapter is hydrogen adsorption and desorption on the normal, reconstructed surface of Si (100) 2x1 (see Figure 10.13). This has been studied very extensively and no attempt is made here to review all of the literature. Rather, selected results will be considered as representative of the behavior of the material.

Hydrogen in its monoatomic form adsorbs very well on Si (100) 2x1. It has been found to produce two different surface phases, one consisting simply of termination of the dangling bonds on the (2x1) surface by H atoms – this phase forms easily and quickly, and a second phase where the Si-Si surface reconstruction bond is broken and two H atoms incorporate into the surface in its place. [12] This disrupts the reconstruction and results in an unreconstructed (1x1) surface. Both of these situations are shown in Figure 10.21. Typically formation of the (1x1) surface requires exposure of the initial clean Si (100) 2x1 surface to more than 1000 L of monoatomic H (more than 1000 atoms arriving per surface site).

Monoatomic H may be produced by passing H_2 gas by a heated W filament or is present, for example SiH_4, which is frequently used as a source gas for Si growth by chemical vapor deposition (CVD, see Chapter 12). When SiH_4 decomposes it leaves a surface covered with H behind. Indeed, it is this process that is in large part the reason for interest in H desorption from Si – it is a necessary step in CVD deposition of Si from SiH_4. The high sticking coefficient is not surprising perhaps since the Si-H bond is actually stronger than a Si-Si bond. Of course hydrogen is normally supplied as H_2 so one must also consider the energy of that bond when determining

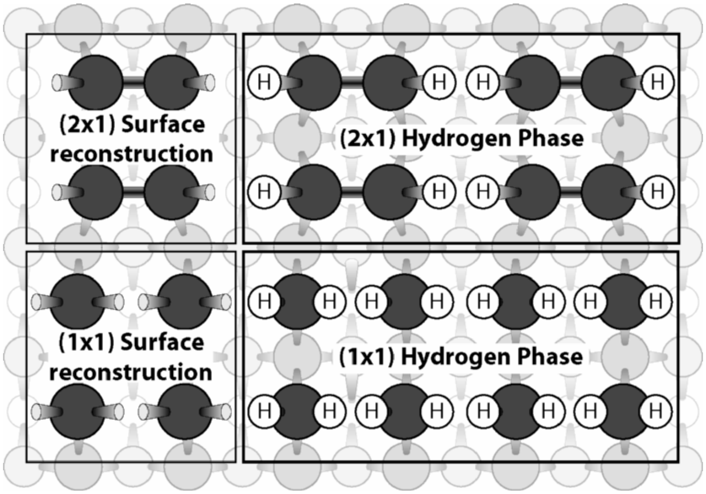


Figure 10.21: A schematic diagram of the Si (100) surface viewed from the top with the 2x1 reconstruction (top half) or with no reconstruction (bottom half). The latter is referred to as a 1x1 surface. The saturation coverage of each of these surfaces with H is shown to the right. The H positions are marked but are schematic and not determined quantitatively.

whether a reaction is endothermic or exothermic. However, in this case we assume that the H_2 is broken apart by another method. Monitoring the valence band structure during the process of H adsorption shows a loss of surface dangling bond states (see Figure 7.29) and an increase in state density at ~10 eV binding energy. [12] Therefore, one can see the elimination of the surface dangling bonds directly.

By contrast, H_2 adsorbs much more weakly with a sticking coefficient on the clean surface following an Arrhenius type behavior. Bratu et al. found an activation energy of 700 meV and a prefactor of 0.1 to 0.01. [13] This behavior is consistent from 275 to 725°C in spite of a very different desorption rate in this range. The same group found that the H_2 sticking coefficient decreases as coverage increases but that previously-adsorbed H is partially catalytic to adsorption such that in addition to the normal effect of loss of available sites for adsorption, the activation energy for adsorption is decreased somewhat. After accounting for this decrease in activation energy the coverage dependence appears to be second order in available surface sites, indicating that H_2 adsorption requires two adjacent open sites for adsorption. For lower temperatures Bratu et al. found based on a review of models and experimental data of their own and of others that adsorption was phonon-assisted, while normal dissociative adsorption occurs at higher temperatures. The behavior of D_2 is similar to that of H_2 with a small increase in adsorption activation energy.

Having adsorbed H_2, one may then consider H desorption. A number of groups have studied this process by a variety of techniques. They generally find that the "monohydride" surface with the 2x1 reconstruction and one hydrogen per dangling bond leads to first order desorption with an Arrhenius behavior having an activation energy of ~2.52 eV and a prefactor of ~10^{15} s^{-1}. [14] H_2 desorbs more easily from the "dihydride" where the surface exhibits the (1x1) reconstruction (Figure 10.21). The activation energy is ~1.88 eV and the prefactor is ~10^{13} s^{-1} for this case and the desorption is second order. [14] Considering that two hydrogens are leaving together, it is surprising that the monohydride surface would exhibit first order desorption kinetics (i.e. the rate is linearly proportional to the H concentration on the surface). A mechanism for this first-order process was proposed by Sinniah et al. [15] in which the first step was formation of an excited Si-H^* bond followed by reaction of the H^* with a normal H atom to form a molecule, which then desorbed. Thus the two-step process was rate limited by a single atom event; hence the first-order behavior. This behavior is consistent with the contention by Bratu [13] that the desorption process is most strongly influenced by the surface vibrational modes.

The adsorption and desorption behaviors of Si (100) 2x1 described above are summarized in Figure 10.22.

For a substrate surface heated at ~2°C per second, most of the dihydride surface will desorb H_2 and convert to a monohydride surface at ~400°C, while the monohydride will desorb H_2 and yield a clean surface at ~520°C. Slower heating or a static anneal will allow to desorption at lower temperatures if sufficient time is available. Hydrogen-terminated Si (100) surfaces can also be created from normal air-exposed oxidized surfaces by dipping the wafer in HF. The strength of the Si-H bond is illustrated by the observation that this surface is stable in laboratory air under standard conditions for several minutes to several hours.

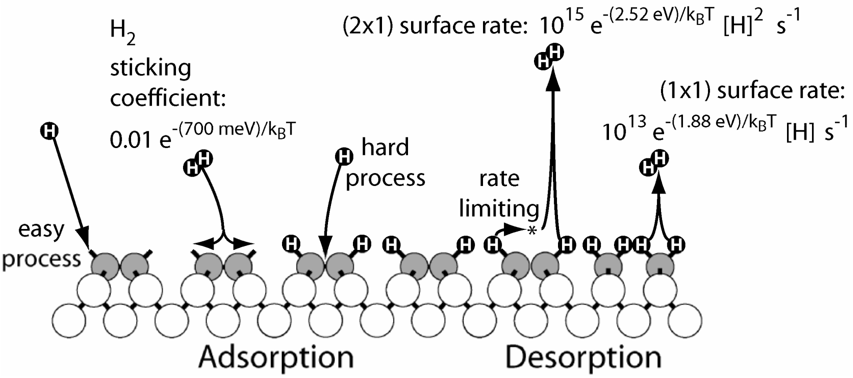


Figure 10.22: A schematic diagram summarizing the hydrogen adsorption and desorption mechanisms on Si (100) 2x1. The excited state for H_2 desorption from the 2x1 surface is indicated with a "*". H incorporation into dimer bonds is slow.

10.12.2 Surface processes in GaAs epitaxial growth

A more complicated situation than H on Si is GaAs. Indeed, this case is so complicated, having many differences as a function of growth properties, that here we will only summarize some of the behaviors and refer the reader to the literature for the details. We will consider only epitaxial vapor phase growth of the (100) GaAs surface by molecular beam epitaxy (MBE) (see Chapter 11). The basic surface is shown schematically in Figure 10.23. This surface is chosen here for illustration because it is the technologically important surface and the one that produces the best growth and film properties.

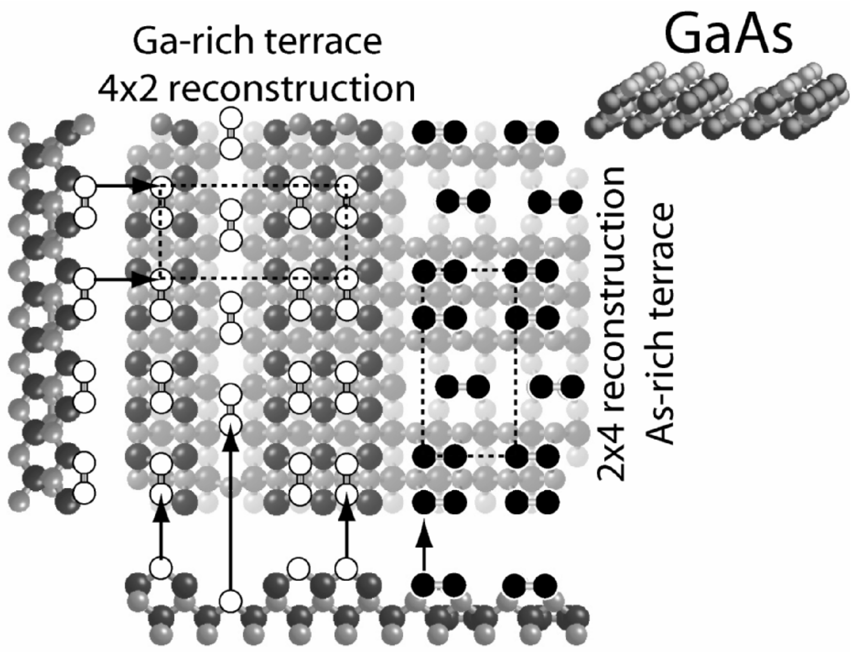


Figure 10.23: Shows the structure of the GaAs (100) surface. The larger darker circles represent As while the smaller lighter circles represent Ga. The top surface atoms in the reconstructed positions are highlighted in white (Ga) and black (As).

There are several points to note about the GaAs (100) surface. First, the surface reconstructs into dimer rows as does silicon (100) 2x1. However the arrangement of these dimers is more complex to account for the difference in chemistry of the anion and cation sites and to get the electron pairing that drives reconstruction correct. The structure removes half of the top layer of atoms and some of the second layer atoms to expose a third layer of the same chemistry as the top layer. These exposed atoms then reconstruct into dimers. The reconstruction is the same for a Ga-terminated surface or an As-terminated surface except that the structure is rotated by 90°. The reconstruction is periodic every second unit cell in one direction and every fourth in the other direction, hence the reconstructions are designated 4x2 and 2x4 for the Ga and As terminated surfaces, respectively.

The basic idea of the growth process is that Ga is evaporated from Ga liquid and arrives at the growing surface as atoms. As is evaporated from sources that produce either As dimers or tetramers. The condensing atoms provide the material from which the film grows. If the temperature is high (above ~650°C) As evaporates from the surface leaving it Ga rich unless a sufficient flux of As is available to counter-balance evaporation. Even at lower temperatures some evaporation occurs and some As is required. If evaporation is sufficiently rapid Ga will accumulate on the surface leading to formation of Ga droplets. This is very bad for growth of a good crystal. Ga can also evaporate from the surface but this process is essentially the same as for evaporation of Ga from its own metal surface (see the vapor pressure curves for Ga) and only happens when the surface is much hotter than during normal epitaxial crystal growth. Ga evaporation varies slightly depending upon the flux of As arriving at the surface at the same time. Normally one does not have to worry about Ga evaporation.

The balance between evaporation and condensation of Ga and As determines whether the surface is Ga rich or As rich. The question of whether the surface is Ga rich or As rich is critical to the growth behavior in many other ways and affects the ultimate quality of the grown layer significantly. To understand how the Ga/As ratio is set it is necessary to look at the details of adsorption and desorption primarily of As. Some of the behaviors are illustrated in Figure 10.24. In practice one can determine the cross-over from Ga rich to As rich by the transition from a (2x4) to a (4x2) reflection electron diffraction pattern (see Chapter 11) as one adjusts the As flux.

Arsenic evaporates as a tetramer, As_4, from its own surface. Therefore in MBE where simple effusion sources (see Chapter 11) are used to supply arsenic to the growth surface, the primary arriving species is As_4. This physisorbs weakly on the Ga-rich GaAs surface with a binding energy of ~260 meV [16] and does not adsorb detectably on a completely As-covered GaAs surface at normal GaAs growth temperatures. The weakly adsorbed tetramers can migrate across the surface with an activation energy of ~250 meV. [17] Note that the migration activation energy is very close to the adsorption/desorption energy so desorption is roughly as likely as surface migration. However, if the molecule can find a pair of open Ga surface sites it can chemisorb (without decomposing) with a higher binding energy of ~380 meV. [17]

It has been proposed and argued based on experimental results that decomposition of As_4 to deposit single As atoms on the surface requires multiple open Ga surface sites.

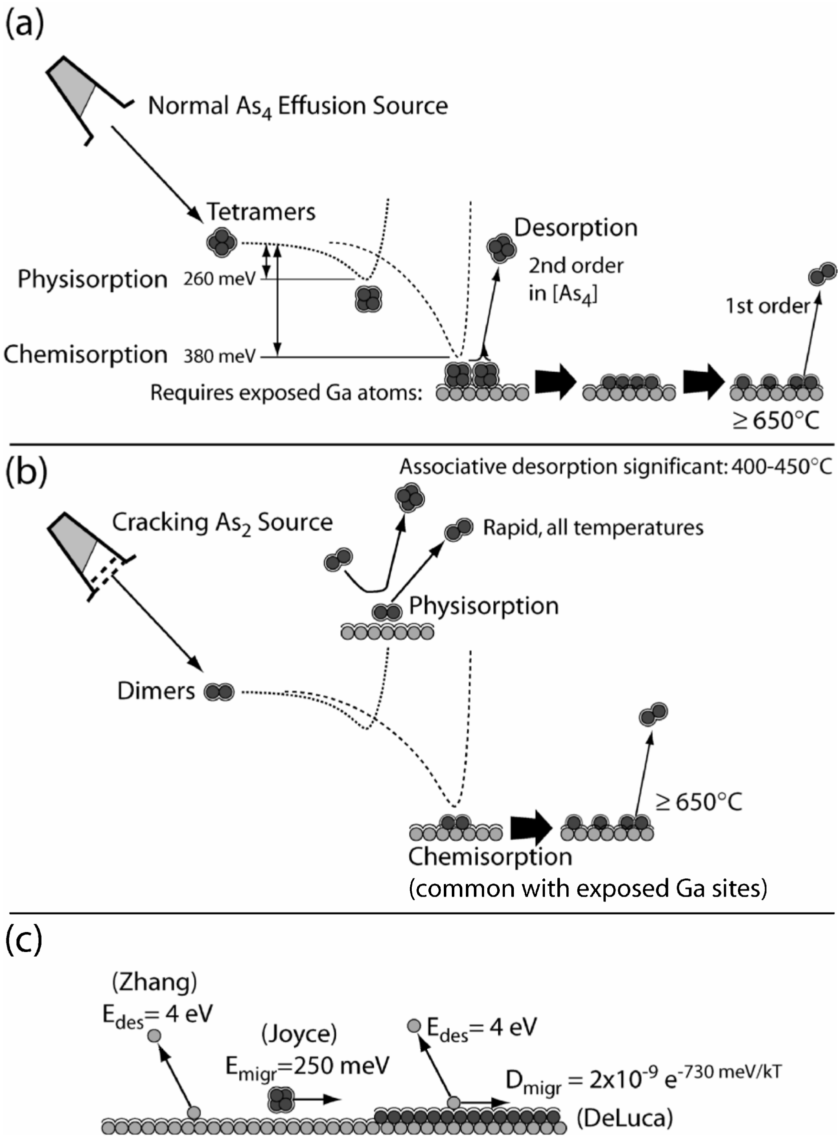


Figure 10.24: Some of the processes involved in (100) GaAs epitaxial growth from the vapor phase. Data for parts (a) and (b) are from Joyce [17]. Other references are to Zhang [18] and Deluca [19].

Joyce [17] proposed that four open Ga sites are required and that two As_4 molecules must adsorb and migrate such that these four sites that are adjacent and in a specific orientation to one another (later has been referred to as "configuration-dependent reactive incorporation" by Madhukar and others). These two As_4 molecules then react to produce four adsorbed As atoms and release an As_4 molecule. This configuration requirement makes the incorporation probability for As very low on a surface containing few open sites (exposed Ga) so adsorption in the presence of excess As is self limiting.

Understanding why it is difficulty to get As_4 to adsorb on GaAs immediately suggests a possible solution. When As evaporates from a surface that contains relatively few As atoms it comes off as As_2. One can design a cracking effusion source (Chapter 11) that provides As_2 to the growth surface rather than As_4. It was found that As_2 has a very high adsorption probability on Ga-terminated GaAs surfaces with both a weakly-bound physisorbed state and a strongly-bound chemisorbed state. [17] However, there is relatively little barrier to chemisorption if two adjacent open As sites may be found. Therefore, the As_2 incorporation process consists of physisorption on the surface, diffusion, and either desorption within a few microseconds or chemisorption on a pair of open surface sites. At moderate temperatures the physisorbed species may desorb associatively as As_4 but desorption is normally as As_2.

Having considered the adsorption and desorption of Ga and As on the growing surface, we can now briefly consider the growth process. Ga migrates across the GaAs surface anisotropically as might not be surprising from the anisotropic nature of the As- and Ga-terminated surface reconstructions. The preferred surface is the As-terminated where it has a diffusivity along the channels (parallel to the dimer bonds) of: [19]

$$D_{Ga}^{As-ter\min ated} = 2x10^{-9} \quad e^{-730meV/k_BT} \; cm^2 \; s^{-1} \qquad 10.15$$

Diffusion across the channels is roughly four times slower. On the Ga-terminated surface the diffusivity is roughly three six times higher. [20]. Therefore Ga on an open Ga-terminated region will move quickly until it comes to a surface step and moves up or down onto an As-terminated region where diffusion is much slower. Therefore, the As-terminated regions will accumulate most of the free Ga adatoms while As will only stick to the Ga-terminated areas.

Atomic diffusion on GaAs surfaces has been examined in the context of coarsening of surface islands on a flat surface. [21] They and others have found that coarsening does not proceed as one would expect for normal attachment/detachment and diffusion processes on surfaces. The data is consistent with a higher than usual concentration of adatoms on the surface, suggesting that the attachment rate of atoms to surface islands is relatively slow compared to the rate at which atoms leave the clusters. Likewise, it suggests that nucleation of new islands is even slower.

GaAs left to grow in its equilibrium crystal shape tends to produce {110} type facet planes. In some conditions growth even on a {100} type surface will produce such facets but normally the surface remains flat, as faceting to the {110} would increase the surface area more than enough to compensate for the improved facet energy. Therefore the surface tends to be flat. Growth proceeds by diffusion of Ga atoms onto the As-terminated regions. As they accumulate into islands they rapidly become covered with As atoms. Now we can see why there is an advantage in growth conditions that minimize As on the growth surface while maintaining the As-terminated structure. Too much As will tend to trap moving Ga atoms too easily and reduce their effective diffusivity. Too little As will allow the surface to convert to Ga-terminated. Once this occurs it is difficult to avoid droplet formation. Therefore, the optimal growth condition is just enough As_2 to maintain the As-termination but no more.

10.13 SUMMARY POINTS

- Solid phase epitaxy and film growth can only occur when reaction source materials need not diffuse far to react to form the final film, there should be no product species that need to escape from the reaction region.
- Reaction products may be dictated by nucleation or growth stages. Nucleation can depend upon the free energy of the phase forming, interfacial or surface energies, lattice misfit and strain energy, and what reactant is diffusing to form the new phase in the case of a solid phase reaction.
- Vapor phase film growth typically consists of adsorption, desorption, surface diffusion, nucleation, and growth steps.
- Atoms and molecules move substantial distances that increase with decreasing pressure and increasing energy of the moving species.
- The flux of gas particles crossing a plane is linearly related to gas pressure and inversely related to the square root of mass and average kinetic energy.
- The purpose of conducting growth processes and other experiments in ultrahigh vacuum is that the surface remains free of contamination for relatively long periods of time.
- Adsorption processes bond atoms to surfaces through weak interactions such as van der Waals bonds (physisorption) or strong chemical bonds (chemisorption). Each has a separate energy-distance relationship. Getting a molecule to bond to a surface may be limited by the energy and other barriers to transferring to a strong chemisorption configuration.
- Adsorption probability may depend strongly on the chemistry of the surface on which adsorption is to occur.
- Adsorption can depend upon the configuration of available sites on the surface.
- Desorption is a process of evaporating atoms from a surface into the vapor phase. Desorption depends upon the surface temperature, the number of atoms on the surface and how strongly they bind to that surface.
- Higher order desorption processes involve several atoms forming a cluster or molecule and desorbing as a unit. The rate of these processes generally scales with a power of the concentration of desorbing species where the exponent of the power is the number of atoms/particles of one type that must join together for desorption to occur.
- The number of atoms of a given type desorbing as a cluster from a surface may depend upon the chemical nature of that surface.
- The steady-state coverage of species on a surface depends upon their arrival rate, their adsorption probability, and their surface residence time.
- Thin film nucleation can often be described as a series of steps of attachment of atoms to each other to form a cluster and then attachment and detachment of atoms from the clusters. The attachment and detachment rates are affected by the energy change associated with adding an atom to the cluster.

- If single atoms do not stick together well or nucleation requires a large density of atoms and if isolated atoms on the surface desorb relatively easily a nucleation delay may result.
- Denuded zones in which no nucleation generally occurs surrounds existing nuclei on surfaces because the nuclei sweep the nearby area clean of atoms, which are required for further nucleation.
- Coarsening is a process in which atoms transfer between clusters. Because larger clusters are generally favored the transfer process is typically faster from small clusters to large clusters causing the small clusters to shrink and the large clusters to grow.
- Surface diffusion is faster than bulk diffusion and may be highly anisotropic due to surface structure.
- Energy barriers favoring or opposing transfer of atoms across surface steps and the energy binding or repelling an atom from step edges has a strong influence on surface morphology.
- Different surface crystal planes have different energies, often influenced by surface reconstructions and surfactants.
- Crystal growth may favor the lowest energy surface for thermodynamic reasons or the lowest energy or other surface planes may be favored because that plane grows more rapidly than others.
- Relative surface and interface energies determine the contact angle at which the film prefers to intercept the substrate surface.
- Thin films may form as two-dimensional films if they have a close lattice match to a substrate and if they lower the surface energy. (Lattice match may not matter if one is not growing the films as epitaxial layers.)
- Thin films generally nucleate as three dimensional islands when they raise the surface energy as they form or if they have a large lattice mismatch with the substrate or both.
- Films form by the Stransky-Krastanov mechanism (a flat layer across the substrate only a few atom layers thick followed by three dimensional islands) if the film lowers the surface energy but where there is a large lattice mismatch with the substrate.
- When a film has no specific reason to prefer one surface orientation over another on a substrate it tends to form surfaces consisting of close packed planes during film nucleation.
- The surface orientation after growth of a film for some time may change from that originally nucleated, for example by preferential growth of grains with other orientations.
- Residual stress in a growing film is typically tensile when the film has a columnar microstructure with small voids between crystalline columns.

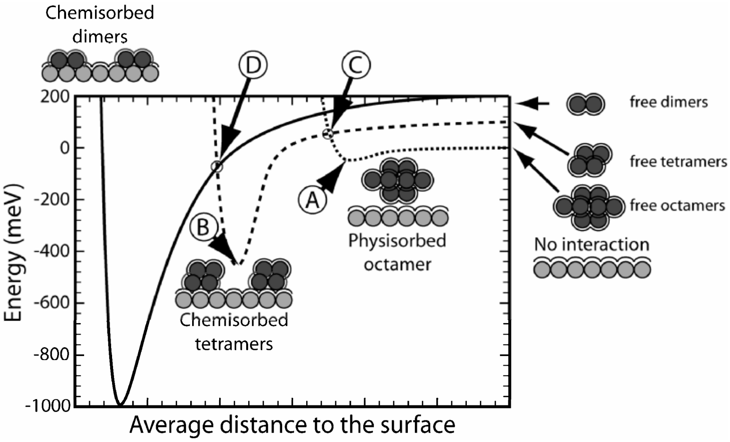
- Residual stress may be made more compressive by bombarding the film with energetic particles as it grows.
- Differential thermal expansion affects residual stress in films.
- Segregation of impurities to surfaces may be driven by a desire to lower surface energy or because the impurity is much larger than the site into which it would need to incorporate in the bulk solid or both.

10.14 HOMEWORK PROBLEMS

1. Suppose that an evaporation system has a distance from an effusion source to the substrate of 30 cm. To prevent any significant scattering of gas during the movement of atoms from source to substrate you want at least three mean-free-path lengths over this path. Assume that the collision cross section is $\sigma \sim 4\text{x}10^{-15}$ cm^2.
   a) Based on Equation 10.1, what is the maximum acceptable pressure in the evaporation system if the gas temperature is 300K?
   b) By the same method, what is the maximum acceptable pressure if one is evaporating Ga atoms at a temperature of 1000 K?

2. To grow a GaAs film at a rate of 1 ML s^{-1} you require a flux of $5\text{x}10^{14}$ Ga atoms and $2\text{x}10^{16}$ As_4 molecules arriving at the substrate surface per square centimeter per second. Assume that the Ga mass is 69.7 AMU, the As_4 mass is 300 AMU, and the source temperatures are 1000 and 500 K for Ga and As, respectively.
   a) Using Equation 10.4, calculate the beam equivalent-pressures to achieve the two fluxes needed for As and Ga.
   b) Using the cross section $\sigma \sim 4\text{x}10^{15}$ cm^2, the temperature being the Ga temperature, the pressure is that of As_4 (assumed constant throughout the system), calculate the mean free path for Ga atoms passing through the As_4 vapor.
   c) Would you expect the As_4 vapor to scatter the Ga atoms significantly?

3. You are growing the hypothetical II-VI semiconductor CA by evaporation of A_8 octamers from an effusion source. Chemisorption requires open sites for all of the adsorbing A atoms. Suppose that the A_8 molecule chemisorbs as in the figure:



Where the energies at the marked points are:

A: –25 meV
B: –500 meV
C: +50 meV
D: –50 meV

Other important energies are:

Energy of a free octamer:	0	meV
Energy of a free tetramer:	+100	meV
Energy of a free dimer:	+200	meV
Energy of a chemisorbed dimer:	–1000	meV

Assume that the rates of processes go as concentrations multiplied by Boltzmann factors. For example, the rate of crossing the barrier for a tetramer to convert to adsorbed dimers is proportional to:

$$r_{TD} = C_T e^{-450\,\mathrm{meV}/k_B T},$$

where C_T is the concentration of surface tetramers. The rate of desorption of the tetramer would be:

$$r_{desT} = C_T e^{-600\,\mathrm{meV}/k_B T}.$$

a) Based on this assumption and the energies given and that there is no rate limitation to crossing from one curve to another at the crossing points, estimate the relative rate of octamers converting to tetramers relative to the number desorbing from the surface at the growth temperature of 400°C.
b) Likewise, calculate the relative rates (at equal concentrations) of:
    i. Tetramers to dimers relative to tetramer desorption.
    ii. Tetramer desorption to octamer desorption.
    iii. Dimer desorption to octamer desorption.
c) Taking the result in (a) divided by the quantity one plus the results of (b.ii) and (b.iii), estimate the sticking coefficient for A_8 octamers on the growth surface. [Do the results in part (b) make a significant difference to the result?]
d) Recalculate the sticking coefficient at 200°C.
e) If the dimers desorb as tetramers from the surface, and if the dimers move together as dimers rather than moving as single adatoms, what would you expect the concentration dependence of desorption to be? [For example, the equation above for r_{desT} is proportional to the first power of tetramer concentration.]

4. You are depositing In metal on a glass slide.
   a) If you increase the temperature of the deposition would you expect the denuded zone around an island to increase or decrease in size.
   b) Suppose that the surface energy of the glass slide is 2.5 times greater than that of the In and that the interface energy is twice as great as the In. Calculate the contact angle you would expect for the In islands.
   c) If you were able to decrease the surface energy of the glass by a factor of two without affecting the interface energy through the application of a surfactant how would you expect the contact angle to change?
   d) Would you expect reconstruction of a semiconductor surface to raise or lower the surface energy? (Briefly justify your answer.)

5. You are depositing a thin film of InP on two different substrates, Si and Ge. The thermal expansion coefficients and lattice constants are:

	Thermal expansion Coefficient $°C^{-1}$	Lattice constant nm
Si:	$2.6\text{x}10^{-6}$	0.5431
Ge:	$5.9\text{x}10^{-6}$	0.5658
InP:	$4.6 \text{ x } 10^{-6}$	0.5687

   a) Under growth conditions if the film is stress free, then upon cooling what is the sign of the stress of the InP grown on a Ge and on a Si substrate? (i.e. compressive or tensile)
   b) If the growth temperature is 600°C and if the film is strain free at this temperature, what is the magnitude of the strain at 20°C? (Strain is unitless.)
   c) If the strain in the film is determined by the lattice misfit at the growth temperature, which substrate would be the better choice as a substrate to minimize strain upon cooling? (Assume that thermal expansion strain directly offsets misfit strain.)

10.15 SUGGESTED READINGS & REFERENCES

Suggested Readings:

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