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Growth Kinetics of Thin Film Epitaxy

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Abstract

This chapter mainly introduces five basic stages of the film deposition process (vapor adsorption, surface diffusion, reaction between adsorbed species, reaction of film materials to form bonding surface, and nucleation and microstructure formation), analyzes the influence of deposition process parameters on the three basic growth modes of the film, focuses on the relationship between the control parameters of homoepitaxy and heteroepitaxy and the film structure, gives the dynamic characteristics of each growth stage, and examines the factors determining epitaxy film structure, topography, interfacial properties, and stress. It is shown that two-dimensional nucleation is a key to obtain high-quality epitaxial films.

Keywords: deposition, adsorption, diffusion, nucleation, epitaxy, dynamic characteristics

1. Introduction

Epitaxial thin films and artificial multilayers are grown on solid single-crystal surfaces with atomic monolayer thickness control either by chemical vapor deposition (CVD) [1, 2] or by molecular beam epitaxy (MBE). In CVD, precursor molecules are thermally decomposed in a continuous flow oven in a background atmosphere of clean inert gas, whereas in MBE the surface is held in ultrahigh vacuum (UHV, 10^{-8} Pa). Controlling the growth morphology is a challenge in both fabrication techniques; it requires knowledge of both thermodynamics and of kinetics.

As with other thin films, epitaxial films can provide properties or structures that are difficult or impossible to obtain in bulk materials. Indeed, many materials are easier to grow epitaxially than to grow and shape in bulk form. Compared to polycrystalline films, epitaxial films have at least four advantages, which are elimination of grain boundaries, ability to monitor the growth by surface diffraction, control of crystallographic orientation, and the potential for atomically smooth growth.

Epitaxy is the special type of thin film deposition and is particularly demanding about all aspects of process control. Film quality is readily degraded by small amounts of contamination, nonstoichiometry, and lattice mismatch. On the other hand, when good control is achieved, complex multilayered structures with unique properties can be fabricated with atomic layer precision. Moreover, the precise structural and compositional nature of the epitaxial growth surface allows the use of

growth monitoring techniques that give detailed information about film growth mechanisms on an atomic scale.

The purpose of this chapter is to guide the new readers who have just entered this field. Based on the in-depth analysis of the main aspects of epitaxy technology by cross-referencing the relevant literature provided by experts, the research and development direction of epitaxy technology are evaluated. Epitaxy refers to the orderly growth of crystal materials on the substrate crystal and the establishment of a clear crystal relationship at the interface between the two crystal lattices. In homoepitaxy, the epitaxial layer and substrate are made of the same material, while in heteroepitaxy, they are made of different materials. If two materials have the same crystal structure, they are called similar, otherwise they are called different. In the epitaxial structure, the same lattice spacing between the epitaxial material and the substrate material in the same direction plane is called lattice matching, otherwise, lattice mismatch. At one growth site, the constituent atoms are bonded to the epitaxial film, in which the bonding leads to the unequal probability of the atoms' attachment and desorption in the equilibrium. Atoms bonded with energy higher than the growth site are considered to be part of the epitaxial film. All atoms bonded with less energy than the growth sites are called adatoms. In the region of relatively high temperature, the mobility of atoms is stronger, and they can aggregate into two-dimensional islands, thus forming a new surface step. The method of epitaxy can be divided into (1) solid phase epitaxy (SPE), (2) liquid phase epitaxy (LPE), and (3) vapor phase epitaxy (VPE). This chapter only discusses the growth kinetics of each stage, including gas adsorption, surface diffusion, interaction of adsorbed species, bonding of surface-forming film materials, and nucleation and microstructure formation of epitaxial growth, rather than specific epitaxial growth methods.

2. General description of epitaxial growth

In the early study of thin films, it was found that the growth process of thin films is a complex process, including atom arrival, atom adsorption, diffusion/migration on the surface, nucleation, and coalescence. It was also found that four parameters influence the film growth: pressure, deposition rate, substrate temperature, and substrate structure. Also, the binding energy of the adsorbent to the substrate is of vital importance, but since this is not a controllable parameter, we will ignore it here. For metals adsorbed on insulator surfaces, we assume that every atom that impinges on the surface stays there. For other systems one may operate with a sticking coefficient, which is the probability of an atom sticking to the surface upon impingement. The adsorbed atoms can exhibit a complicated dynamical behavior at the surface: Atoms can move around on the corresponding surface, and they can diffuse into the substrate or even desorb from the substrate. When two atoms meet, they form metastable nuclei. This is referred to as nucleation. Nuclei can also split up, rotate, or migrate across the surface. At a certain critical size, the nuclei become stable, and this is where actual crystal growth begins. Initial film growth is categorized into three different types of behaviors. The three growth modes are called Volmer-Weber (VW), Stranski-Krastanov (SK), and Frank-van der Merwe (FM) [3]. **Figure 1** illustrates the different growth modes, which can be described as follows. For VW growth the growth is occurring as three-dimensional (3D) nuclei

Figure 1.

Illustration of the three different growth modes. Left: FM growth. Center: SK growth. Right: VW growth.

which later coalesce. SK growth is characterized as the formation of one or more layers upon which nucleation and growth dominate. FM growth or layer-by-layer growth is the growth mode that has our interest because of the well-ordered surfaces produced this way. To achieve layer-by-layer growth of atoms, instead of 3D growth, one must try to reduce the nucleation rate. This can be done by (1) reducing the pressure since it is believed that residual gases can create nucleation sites on the substrate surface, (2) increasing the substrate temperature which promotes the mobility of the atoms on the surface, or (3) reducing the deposition rate. RHEED can be used to verify the growth mode because oscillations of the intensity indicate that layer-by-layer growth is occurring.

Firstly, the heart of the thin film process sequence will be discussed. Deposition may be considered as six sequential substeps, and that will be examined one by one in the next section. The arriving atoms and molecules must first (1) adsorb on the surface, after which they often (2) diffuse some distance before becoming incorporated into the film. Incorporation involves (3) reaction of the adsorbed species with each other and the surface to form the bonds of the film material. The (4) initial aggregation of the film material is called nucleation. As the film grows thicker, it (5) develops a structure, or morphology, which includes both topography (roughness) and crystallography. A film's crystallography may range from amorphous to polycrystalline to single-crystal. The last is obtained by epitaxy—that is, by replicating the crystalline order of a single-crystal substrate. Epitaxy has special techniques and features which are also the focus of this chapter, and (6) diffusional interactions occur within the bulk of the film and with the substrate. These interactions are similar to those of post-deposition annealing, since they occur beneath the surface on which deposition is continuing to occur. Sometimes, after deposition, further heat treatment of a film is carried out to modify its properties. For example, composition can be modified by annealing in a vapor, and crystal growth can be achieved by long annealing or by briefly melting. These post-deposition techniques will not be discussed in this chapter.

The word “epitaxy” comes from the Greek word *epi*, which means “located on,” while “*taxis*” means “arranged.” Epitaxial growth refers to the registration or alignment of the crystal atoms in the single-crystal substrate into the single-crystal film. More precisely, if the atoms of the substrate material at the interface occupy the natural lattice position of the film material, the interface between the film and the substrate crystal is epitaxial, and vice versa. These two materials do not have to be the same crystal, but they are usually like this. When the film material is the same as the substrate material, the crystallographic registration between the film and the substrate is usually called uniform epitaxy. The epitaxial deposition of thin film materials different from substrate materials is called heteroepitaxy.

Epitaxial growth technology has important advantages in material manufacturing of microelectronic and optoelectronic applications. It can be used to prepare films with very good crystal quality. This also makes it possible to fabricate composite films with ideal electronic or optical properties that do not exist in nature. There are many factors that affect the selection of materials and processing methods for epitaxial growth. It includes the chemical compatibility of the film material and the substrate material; the magnitude of the energy band gap of the film material and its relationship with the energy band gap and the edge of the energy band of the substrate material; whether the minimum value of the conduction band energy and the maximum value of the valence band energy are in the same wave vector position is an important factor in optical applications; and the chemical compatibility of the dopant applied to produce the required functional behavior.

In heteroepitaxial film growth, the substrate crystal structure provides a template for locating the atoms of the first arriving film material, and each atomic layer

of the film material provides the same function for the next layer formed by FM growth, as described in the previous section. If the substrate is a single crystal with good quality and the vapor supersaturation is moderate, the atoms have a high mobility on the growth surface; this is a common growth mode. If the lattice parameter mismatch is not too large, for example, it is less than 0.5%, the growth tends to plane. If the mismatch is large, the material tends to gather on the surface of the island, but remains epitaxial.

Plane growth is carried out by attaching atoms to the edge of the step, which causes the step to move on the growth surface. Generally speaking, the unstressed lattice size of the thin film material in the direction parallel to the interface, such as a_f , will be different from the lattice size of the substrate, such as a_s ; this difference may be as high as a few percent. However, the atomic position of the thin film material is consistent with that of the substrate, and the atomic structure of the thin film material is maintained. The thin film material bears any necessary strain along the interface, which makes it possible. In terms of lattice parameters, this mismatch strain is:

$$\epsilon_m = \frac{a_s - a_f}{a_f} \tag{1}$$

The definition of mismatch strain in Eq. (1) is consistent with the standard definition of tensile elastic strain of material in the state of no stress. Sometimes we use the denominator of a_s instead of a_f to measure the lattice mismatch. In this case, the value of the mismatch strain is slightly different. The definition in Eq. (1) is consistent with the concept of tensile strain, i.e., the change of material element length relative to the initial length, which will be used in all cases here. The process of epitaxial film growth is shown schematically in **Figure 2**. Although this process will lead to the potential large elastic strain in the film, for very thin film, the energy

Figure 2. Schematic illustration of heteroepitaxial film growth with lattice mismatch. The substrate thickness is presumed to be large compared to film thickness, and the structure extends laterally very far compared to any thicknesses. Under these circumstances, the lattice mismatch is accommodated by elastic strain at the deposited film.

cost of adding strain material is easily offset by the energy gain associated with the potential chemical bonding effect in the process. This can be proved by a simple argument, which only depends on the familiar block parameter value.

Take a simple comparison of different forms of energy. Both the elastic energy and the bonding energy can be compared with kT_s (Boltzmann constant times the absolute temperature of the substrate). This quantity is an indicator of the average energy per adatom in the substrate. At a typical deposition temperature of 800 K, the value of kT_s is about 0.07 eV. Interestingly, this value is one order of magnitude smaller than the bond energy estimate, but one order of magnitude larger than the elastic energy estimate. Although these are rough estimates, the calculation is instructive.

3. Dynamic characteristics of each stage of epitaxial growth

3.1 The process from vapor to adatoms

In this section, the factors controlling the early growth of thin films on the substrate are described from the perspective of atomism. This process starts with a clean surface of the substrate, which at a temperature of T_s is exposed to the vapor of the chemically compatible film material, which is at a temperature of T_v . In order to form a single-crystal film, the film material atoms in the vapor must reach the substrate surface, adhere to it, and locate a possible equilibrium position before the structural defects remain in the growth front. On the other hand, in order to form amorphous films, it is necessary to prevent atoms from reaching the growth surface to obtain a stable equilibrium position. In both cases, this must occur in a more or less identical way over a very large area of the substrate surface for structural development. At first glance, the result seems unlikely, but such films are made as usual. The atoms in the vapor touch the surface of the substrate, where they form chemical bonds with the atoms in the substrate. The idea that the temperature of the substrate must be sufficiently low so that the vapor phase is in a sense super-saturated with respect to the substrate will make the following more specific. In the process of adhesion, energy is reduced due to the formation of bond. As shown in the diagram in **Figure 3**, if the energy generated due to thermal fluctuation is enough to overcome the adhesion energy occasionally, some parts of the adhesion atom (called the adsorption atom) can be returned to vapor by evaporation.

Figure 3.
Schematic showing the atomistics of film formation on substrates.

In order to make the discussion more specific, we assume a simple hexagonal close-packed crystal structure to facilitate the calculation of bonding. It has been recognized that in order to make the film growth possible, the vapor contacting the growth surface must be supersaturated with respect to the substrate at the substrate temperature T_s . For a uniform crystal at a certain temperature in contact with its own vapor at the same temperature, the equilibrium vapor pressure p_e of the system is defined as the pressure under which the vapor atoms condense on the solid surface and the atoms evaporate from the surface at the same rate. In equilibrium, the entropy free energy of each atom in the vapor is equal to the free energy of each atom in the crystal. Due to the effect of chemical bond, the lower internal energy of atoms in the crystal is offset by the lower entropy energy in the crystal. For the net deposition of the substrate surface, the pressure p in the vapor must be higher than the equilibrium vapor pressure p_e at the substrate temperature, that is, the vapor must be supersaturated. For pressure p , the entropy free energy of each atom in the vapor, which is higher than the pressure p_e , is estimated as the work of each atom required to increase the vapor pressure from p_e to p at a constant temperature. According to the ideal gas law, $kT_v \ln p/p_e$ where $k = 1.38 \times 10^{-23}$ J/K = 8.617×10^{-5} eV/K is Boltzmann constant, T_v is the absolute temperature of the vapor. If the vapor becomes supersaturated, there is a difference of free energy between the vapor and the crystal, which provides the chemical potential of the interface driving the interface toward the vapor. As the interface progresses in a self-similar way, some distant layers of vapor of the same mass are transformed into inner layers of the same mass. When these energies are the same, the interface will not move forward or backward.

In thin film deposition, because the vapor phase and the substrate are not the same material phase, and the temperature of the substrate is usually lower than that of the vapor phase, the situation is often complex. In this case, the definition of equilibrium vapor pressure is not clear. However, in most cases, when the vapor pressure is lower than the equilibrium vapor pressure, the film material will not deposit on the growth surface, which is an operational definition of p_e in the film growth process. Once atoms are attached to the substrate, their entropy free energy will be reduced from that of the vapor. These atoms form a two-dimensional vapor distribution on the substrate surface. The deposited material will be rapidly heated to the substrate temperature T_s . On the surface of the crystal, there are some atoms whose density ρ_{ad} is balanced with a straight surface step or wall frame adjacent to some monolayer atoms, that is, the step does not move forward or backward. Step is the boundary between two phases in a homogeneous material system. Therefore, the concept of equilibrium vapor pressure or equilibrium vapor pressure density ρ_{ad}^e can be called in a similar way. In order to realize the film growth by condensation, the free energy of each atom in the two-dimensional gas must exceed the free energy of the fully entrained surface atom, the amount of which is:

$$\varepsilon_{phase} = kT \ln(\rho_{ad}/\rho_{ad}^e) \quad (2)$$

Consider a molecule approaching a surface from the vapor phase, as shown in **Figure 4**. Upon arriving within a few atomic distances of the surface, it will begin to feel an attraction due to interaction with the surface molecules. This happens even with symmetrical molecules and with inert gases, neither of which has dipole moments. It happens because even these molecules and atoms act as oscillating dipoles, and this behavior creates the dipole-induced-dipole interaction known as the Van der Waals force or London dispersion force. Polar molecules, having permanent dipoles, are attracted more strongly. The approaching molecule is being attracted into a potential well like the one that was illustrated in **Figure 5** for condensation.

Figure 4. Adsorption processes and quantities. a , is used only for condensation (adsorption of a material onto itself). A vertical connecting bar denotes a chemical bond.

Figure 5. Molecular potential energy diagram for evaporation and condensation.

Condensation is just a special case of adsorption in which the substrate composition is the same as that of the adsorbate. This is sometimes the case in thin film deposition and sometimes not. In either case, the molecule accelerates down the curve of the potential well until it passes the bottom and is repelled by the steeply rising portion, which is caused by mutual repulsion of the nuclei. If enough of the molecule’s perpendicular component of momentum is dissipated into the surface during this interaction, the molecule will not be able to escape the potential well after being repelled, though it will still be able to migrate along the surface. This molecule is trapped in a weakly adsorbed state known as physical adsorption or physisorption. The fraction of approaching molecules so adsorbed is called the trapping probability, δ , and the fraction escaping (reflecting) is $(1 - \delta)$ as shown in **Figure 4**. The quantity δ is different from the thermal accommodation coefficient, η , which was defined by Eq. (3):

$$\eta = \frac{T_{rs} - T_{rh}}{T_{rs} - T_h} \tag{3}$$

η represents the degree to which the molecule accommodates itself to the temperature T_h of the surface from which it is reflected. Gas-conductive heat transfer is shown in **Figure 6**.

In general, a molecule is at least partially accommodated thermally to the surface temperature, T_s , even when it is reflected without having been trapped.

In addition to the low temperature T , the physical adsorption molecules are mobile on the surface; as shown in **Figure 4**, the adsorption molecules hop (diffuse) between the surface atomic sites. Adsorption molecules can also be desorbed by obtaining enough energy at the tail of thermal energy distribution, or they can form chemical bonds through further interaction with surface atoms, namely, chemical adsorption. If both adsorption states exist, the physical adsorption state is called precursor state. Chemical adsorption involves the sharing of electrons on the new molecular orbital, which is much stronger than physical adsorption. Physical adsorption only involves dipole interaction. These two types of adsorption can be distinguished in almost all gas phase surface combinations, so they constitute a valuable model for analyzing any surface process. This model [4] has long been applied to heterogeneous catalysis, thin film deposition, and condensation of molecular vapors. Recent theory indicates that even the condensation of a monatomic vapor such as Al can involve both adsorption states, the precursor state in that case being an $Al - Al$ dimer whose bonding to the bulk Al is inhibited by the existence of the dimer bond [5]. In such a case, and in the case of condensing molecular vapors such as As_4 , the vapor would not be considered actually condensed until it had become fully incorporated into the solid phase by chemisorption. Thus, the condensation coefficient, α_c , defined by $J_c = \alpha_c J_i$ [J_i , impinging flux; J_c , the portion of J_i that condenses; α_c , corresponding condensation coefficient] is that fraction of the arriving vapor that becomes not only trapped but also chemisorbed, as indicated in **Figure 4**. However, the term α_c is not used in the case of chemisorption on a foreign substrate. Then, the chemisorption reaction probability, ξ , will be derived later. The precursor model may also be applied to cases where both of the adsorption states involve chemical bonding, but where the bonding in one state is weaker than in the other.

These examples will be revisited after a more detailed study of the energetics of the precursor adsorption model.

Consider a hypothetical diatomic gas phase molecule $Y_2(g)$ adsorbing and then dissociatively chemisorbing as two Y atoms. **Figure 7** shows a diagram of the potential energy versus molecular distance, z , from the surface. This is similar to **Figure 5** for condensation except that we have changed from the molecular (ϵ_p) to the molar (E_p) quantities of potential energy which are more conventional in chemistry. The energy scales shown represent typical bond strengths. Three curves are shown: two alternate ones for the precursor state (a and b) and one for the

Figure 6.

Gas-conductive heat transfer between parallel plates at (a) low and (b) high Knudsen numbers, K .

Figure 7.
 Energetics of the precursor adsorption model. Energy scale is typical only.

chemisorbed state (c). By convention, the zero of E_p is set at the E_p of the element Y in its thermodynamic standard state, which we specify for this element to be the diatomic molecule in the gas phase. In fact, all gaseous elements except the inert gases have diatomic standard states. Note that lifting atomic Y out of its potential well along curve c results in a much higher E_p in the gas phase, which corresponds roughly to the heat of formation, $\Delta_f H$, of $2Y(g)$ from $Y_2(g)$. [$\Delta_f H$ usually can be found in thermodynamic tables] [6–8]. The result of this high E_p for $Y(g)$ is that curves a and c intersect at positive E_p , meaning that there is an activation energy, E_a , to be overcome for $Y_2(g)$ to become dissociatively chemisorbed. For the deeper precursor well, b, chemisorption is not “activated,” though there still is a barrier, as shown. The level of E_{ra} or E_{rb} and hence of E_s is determined by the degree to which the bonds within both the precursor and the surface must be strained from their relaxed condition before new bonds can be formed between the precursor and the surface.

There are two ways in which vapor can arrive at the surface having an $E_p > 0$. Gaseous molecules have their E_p raised by becoming dissociated. Solids and liquids have it raised by evaporating. If the E_p of the arriving vapor is high enough, curve c is followed, and direct chemisorption can occur without involving the precursor state. In the language of surface chemistry, direct reaction between an incoming species and a surface site or adsorbate is called the Eley-Rideal mechanism, whereas reaction among surface species is called the Langmuir-Hinshelwood mechanism.

A principal advantage of the energy-enhanced deposition processes is that they can provide enough energy so that the arriving molecules can surmount the E_a barrier and adsorb directly into the chemisorbed state. In other words, the arriving molecules immediately react with the surface to deposit the film. In sputter deposition, species arrive having kinetic energies of around 1000 kJ/mol as well as having $E_p > 0$ by having been vaporized. In plasma-enhanced deposition, vapor molecules become dissociated in the plasma and thus arrive along curve c, above the E_a barrier. Thus, an energy-enhanced process can supply E_a to the arriving species either as kinetic energy of accelerated molecules or as potential energy of dissociated ones.

Conversely, in thermally controlled deposition processes such as evaporation and CVD, the vapor often adsorbs first into the precursor state, that is, it falls to the bottom of the well on curve a or b. Thence, it may either chemisorb by overcoming the barrier $E_{r(a,b)}$ shown in **Figure 7** or it may desorb by overcoming the heat of

physisorption, which is roughly $E_{d(a,b)}$. The competition between these two reactions results in a net rate of chemisorption whose behavior we would like to describe, since it is the basic film-forming reaction. We start with the conventional expression for the rate of a first-order chemical reaction, first-order meaning that rate is proportional to the concentration of one reactant; thus, $R_k = k_k n_s = k_k n_{s0} \Theta$, where R_k = rate of the k th surface reaction per unit surface area, $\text{mc}/\text{cm}^2 \text{ s}$; k_k = rate constant, s^{-1} ; n_s = surface concentration of reactant, mc/cm^2 ; n_{s0} = monolayer surface concentration, mc/cm^2 ; Θ = fractional surface coverage by reactant.

3.2 Diffusion of adsorbed atoms on substrate surface

Surface diffusion is one of the most important determinants of film structure because it allows the adsorbing species to find each other, find the most active sites, or find epitaxial sites. Various methods have been applied to measure surface diffusion rates of adsorbed molecules. The role of surface diffusion in thin films has mainly been inferred from observations of film structure. Scanning tunneling microscope (STM) gives us the extraordinary power to directly observe individual atoms on surfaces in relation to the entire array of available atomic surface sites. STM observation of the diffusion of these atoms should ultimately provide a wealth of data relevant to thin film deposition.

The expression of the surface diffusion rate will be derived using the absolute reaction rate theory [9]. Although this approach cannot provide a quantitative estimate of the diffusion rate, it will provide valuable insight into what factors determine this rate. **Figure 7** showed that adsorbed atoms or molecules reside in potential wells on the surface, but it did not consider the variation in well depth with position, x , along the surface. **Figure 8a** shows that this depth is periodic, or corrugated, with a potential energy barrier of height E_s between surface sites. The top of the barrier is considered to be the “transition state” between surface sites, in

Figure 8. Surface diffusion: (a) potential energy vs. position x along the surface and (b) typical adsorption sites on a surface lattice.

the language of reaction rate theory. **Figure 8b** illustrates a typical adsorbate situation leading to this corrugation. It is a hexagonally close-packed surface lattice on which the adsorption sites are the centers of the triangles of surface atoms and the transition state is the “saddle point” between them. Other bonding situations can lead to the adsorption sites being other points, such as the centers of the surface atoms. In the process of surface diffusion, the bond between adsorbate and surface should be partially destroyed, so that the adsorbate can migrate to the adjacent surface and form a new bond there. This process can be regarded as the basic form of chemical reaction, because any reaction involves the partial fracture of reactant bond and the formation of product bond when the atom moves through the transition state. Therefore, the principles discussed below apply to any chemical reaction, including those occurring in CVD.

There will be some flux, J_s (mc/cm s), of adsorbate across the E_s barrier between sites 1 and 2 in the x direction of **Figure 8b**. The flux here is in surface units, which are per linear cm of crosswise distance, y , instead of the previously encountered volume flux units, which are per cm² of cross-sectional area. If the distance between sites is a , then the rate of barrier crossing by transition state molecules, per unit area of surface, is:

$$R_s = J_s/a \text{ (mc/cm}^2 \cdot \text{s)} \quad (4)$$

Considering the adsorbate to be a two-dimensional gas at thermal equilibrium, the Maxwell-Boltzmann distribution applies to these translating molecules. Thus, we may use $J_i = \frac{1}{4}n\bar{c}$ for the flux of molecules impinging on the barrier and $\bar{c} = \sqrt{\frac{8RT}{\pi M}}$ for the mean speed. Here, for simplicity, we ignore the small changes in the numerical proportionality factors that arise in going from a three-dimensional to a two-dimensional situation. (It turns out that these factors cancel each other, anyway.) Inserting these equations into Eq. $R_s = J_s/a$ (mc/cm² · s), we have:

$$R_s = \frac{1}{4}n_s^*\bar{c}/a = \frac{n_s^*}{a} \sqrt{\frac{RT}{2\pi M}} = \frac{n_s^*}{a} \sqrt{\frac{k_B T}{2\pi m}} \quad (5)$$

where n_s^* (mc/cm²) denotes the surface concentration of adsorbate residing in the transition state. Now we must find the relation between n_s^* and n_s , the latter being the concentration of molecules in adsorption sites. At thermal equilibrium, statistical mechanics says that the concentration of molecules in a given state is proportional to the total number of ways of distributing the available thermal energy around a large system of molecules in that state. For each type of kinetic energy contributing to the thermal energy, the number of ways, Z , is equal to the sum over all of the quantized energy levels, ϵ_j , of the following products: the Boltzmann factor for each energy level times the number of ways of distributing energy at that level (the degeneracy of the level, g). Thus:

$$Z = \sum_j g_j e^{-\epsilon_j/k_B T} \quad (6)$$

3.3 Nucleation

3.3.1 Surface energy

To understand nucleation, the concept of surface energy needs to be introduced. The familiar experiment of drawing a liquid membrane out of soapy water on a wire

ring is illustrated in **Figure 9**. The force required to support the membrane per unit width of membrane surface is known as the surface tension, γ , expressed as N/m in SI units, or more commonly as dynes/cm in cgs units. For a wire of circumference b , the width of surface is $2b$, since the membrane has both an inner and an outer surface. Thus, the total force required to support the membrane is $F = 2b\gamma$. As the membrane is extended upward in the x direction, work $F(\Delta x)$ (N m or J) is done to create the new surface, and the surface area created is $A = 2b\Delta x$, assuming for simplicity a constant membrane circumference. The work is stored as surface energy (as in stretching a spring), so the surface energy per unit area of surface is:

$$F\Delta x/A (\text{N} \cdot \text{m}/\text{m}^2) = (2b\gamma)\Delta x/2b\Delta x = \gamma (\text{N}/\text{m} \text{ or } \text{J}/\text{m}^2) \quad (7)$$

Thus, surface tension (N/m) and surface energy per unit area (J/m^2) are identical, at least for liquids. For solids at $T > 0$ K, surface Gibbs free energy is reduced by an entropy factor [$G = (U + pV) - TS = H - TS$] which depends on the degree of surface disorder. For solids, there is also a quantity called surface stress, which differs from surface energy by a surface elastic strain term. Liquids cannot support such strain, because the atoms just rearrange to relax it.

The surface energy exists because the molecules in the condensed phase attract each other, which is the reason for condensation. The generation of a surface involves the removal of molecular contact (bond breaking) from above the surface, thus involving energy input. Therefore, the movement in the condensed phase can occur within a certain range, and this movement will continue to minimize the total surface energy, γA . In the liquid membrane case, where γ is fixed, this means minimizing A . Thus, when the wire is lifted far enough, the membrane snaps taut into the plane of the ring, and when a bubble is blown, it becomes spherical. In the case of solids, surface energy can be minimized by surface diffusion, which is the basis of the development of film structure. In the film growth, A and γ are varying. Area A depends on the surface morphology, and γ depends on many characteristics of the exposed surface, including chemical composition, crystal orientation, atomic reconstruction, and atomic-scale roughness.

For the deposition on foreign substrates, the substrate γ strongly affects the nucleation behavior. Here, the surface energy γ_s of the free surface of the substrate, the surface energy γ_i of the substrate film interface, and the surface energy γ_f of the free surface of the film should be considered. These three γ values generally depend

Figure 9.
Surface tension of a liquid membrane.

on crystal orientation, passivation, and other factors. It is assumed that there is sufficient surface diffusion to enable the deposited materials to rearrange to minimize γ , i.e., it is assumed that nucleation is not limited by dynamics and can approach equilibrium. For this reason, we must have $\Lambda \gg a$ (Λ is the diffusion length). On the contrary, if $\Lambda < a$, every atom will stick where it falls, and the growth behavior is “quenched.” According to our hypothesis $\Lambda \gg a$, there are two kinds of nucleation on the bare substrate, as shown in the **Figure 10a** and **b**. In **a**, the film diffuses or “wets” the substrate on the substrate because:

$$\gamma_f + \gamma_i < \gamma_s \quad (8)$$

In other words, the total surface energy of the wetted substrate is lower than that of the bare substrate. This leads to the smooth growth of the atomic layer, which is the Frank-van der Merwe growth mode. To achieve this mode, there must be a strong enough bond between the film and the substrate to reduce the γ_i in Eq. (8). If there is no such bond, we will get $\gamma_i = \gamma_f + \gamma_s$, so spreading the film on the substrate will always increase the total surface energy $2\gamma_f$, as shown in the freestanding liquid film in **Figure 9**. Therefore, in the case of insufficient substrate bonding, Eq. (8) cannot be maintained, and the film does not wet the substrate, but forms a three-dimensional (3D) island, as shown in **Figure 10b**, which is called the Volmer-Weber growth mode. There is a third growth mode, Stranski-Krastanov growth mode, as shown in **Figure 10c**. In this mode, due to the change of the energy situation of the continuous single layer, the growth changes from one layer to an island after one or two layers. For liquids contacting solids, the degree of wetting is most easily observed by the rise or depression of a liquid column in a narrow tube (a capillary). Thus, film nucleation analysis in terms of degree of wetting is known as the “capillarity” model. Three-dimensional nucleation is usually undesirable, since it leads to rough, nonuniform films.

Different crystal shapes imply that underlying substrates critically influence the vapor phase growth mode. The substrate-dependent growth characteristics of various low-dimensional nanocrystals in both solution and vapor phase growth have been discussed for their growth mechanisms [10, 11].

Figure 10.
 Film growth modes: (a) Frank-Van der Merwe (layer), (b) Volmer-Weber (island), and (c) Stranski-Krastanov.

3.3.2 Kinetics vs. thermodynamics

In general, within the framework of the nucleation kinetics model [12], a gas phase growth reaction can be divided into two steps: (1) adsorption of vaporized precursors onto substrates and diffusion to the preferential growth sites and (2) incorporation of precursors into existing nuclei. The rate-limiting step in vapor phase crystal growth can be determined as either the diffusion-limited step or the reaction-limited step.

One way to achieve smooth growth is to reduce substrate temperature, T , to inhibit surface diffusion, thus “freezing” the nucleation and coalescence process. If the arriving species do not have enough heat energy to desorb or diffuse, they will stay where they land, leading to the aforementioned quenching growth. In this case, the nucleation process is kinetically inhibited by the surface diffusion activation energy barrier, E_s , in **Figure 8(a)**. This is also the case for ion-bombardment dissipation of 3D nuclei; the nuclei do not have time to reassemble themselves by surface diffusion before they are buried by depositing material.

The question of whether a process is approaching equilibrium or is instead limited by kinetics is an important one, and it arises often in thin film deposition. Process behavior and film properties are profoundly affected by the degree to which one or the other situation dominates. The answer is not always apparent in a given process, and this often leads to confusion and to misinterpretation of observed phenomena. Therefore, to elaborate briefly, the generalized mathematical representation of this dichotomy is embodied in Eq. (9):

$$R_s = R_{-s} \text{ or } n_s k_s = n_s^* k_{-s} \quad (9)$$

where $-s$ denotes the reverse reaction from the transition state back to adsorption site.

Eq. (9) describes the rate balance of a reversible reaction, and Eq. (10) defines its equilibrium constant:

$$K = \frac{k_s}{k_{-s}} = \frac{n_s^*}{n_s} e^{-\Delta_r G^0 / RT} \quad (10)$$

Approach to equilibrium requires the forward and reverse rates to be fast enough so that they become balanced within the applicable time scale, which may be the time for deposition of one monolayer, for example. Then, the concentrations of reactant and product species are related by the difference in their free energies, $\Delta_r G^0$. If, on the other hand, the forward rate is so slow that the product concentration does not have time to build up to its equilibrium level within this time scale, then the product concentration is determined not by $\Delta_r G^0$ but, instead, by the forward rate. This rate is governed by Eqs. (11) and (12):

$$R_k = k_k n_s = k_k n_{s0} \Theta \quad (11)$$

where R_k = rate of the k th surface reaction per unit surface area, mc/cm² s; k_k = rate constant, s⁻¹; n_s = surface concentration of reactant, mc/cm²; n_{s0} = monolayer surface concentration, mc/cm²; Θ = fractional surface coverage by reactant.

$$k_k = v_{0k} e^{-E_k / RT} \quad (12)$$

where v_{0k} = frequency factor or pre-exponential factor; E_k = reaction activation energy, kJ/mol in which E_k/T plays the dominant role. So it is that reactions can be frozen out and equilibration avoided if so desired, by lowering the T .

monolayer (μ_c) may be thought of as the 2D saturation vapor concentration, n_v (mc/m²). If n_s is the actual concentration of the 2D gas, then (n_s/n_v) becomes the 2D supersaturation ratio. By the same procedures as in the 3D case, we may then derive expressions for the critical nucleus as:

$$r^* = \frac{\beta}{a \left(\frac{RT}{V_{mc}} \right) \ln \left(\frac{n_s}{n_v} \right)} \quad (14)$$

and

$$\Delta G^* = \frac{\pi \beta^2}{a \left(\frac{RT}{V_{mc}} \right) \ln \left(\frac{n_s}{n_v} \right)} \quad (15)$$

Here, a is the monolayer thickness. Once supercritical nuclei form, the 2D gas continues to attach to their edges until coalescence occurs and the monolayer is complete. Meanwhile, the next monolayer is beginning to form, and the film continues to build up in this way, atomic layer by layer. In the special case of single-crystal film deposition (epitaxy), the surface may contain many atomic terraces with straight edges as shown in **Figure 11**. The “kink” sites shown in **Figure 11** are also important surface features. Attachment of a 2D gas atom to a random site on the straight edge involves an increase in total edge energy, because it increases the length of the edge. Conversely, attachment to the kink site makes no change in the length of the edge; this is therefore an energetically preferred site, and edge growth can most easily occur by attachment-driven motion of these kink sites along the edge.

It can be seen from the above that the surface energy depends not only on the facet direction discussed in Section 3.3.1 but also on the density of steps and kinks (Williams, 1994). The equilibrium densities of these two features increase with T because of their associated entropy (disorder), S . That is, when the T_s term for the Gibbs free energy, G , becomes larger; the internal energy term, U , also becomes larger to minimize G ; and U here mostly consists of the potential energy of step and kink formation. This is the same T -driven tendency toward disorder that causes vapor pressure to rise with T .

During film deposition, if the surface diffusion rate is high enough and n_s is low enough so that the 2D gas atoms are more likely to attach to an edge than to form a critical nucleus within an atomic terrace, then edge attachment becomes the dominant growth mode, that is, we have $\Lambda > L$, where Λ is the surface diffusion length and L is the distance between terraces. This is called the “continuous” growth mode, as opposed to the nucleated mode. The continuous mode of 2D growth is analogous to the type of 3D nucleation in which nucleation is more likely to occur at active surface sites than by spontaneous nucleation elsewhere on the surface. Active sites and step edges, especially kinked edges, break the nucleation barrier by providing wetting at those sites.

Two-dimensional nucleation is usually preferred to 3D because it leads to smooth growth. In nonepitaxial growth, large grain size (coarse nucleation) may be desired in addition to smoothness. Unlike in the 3D nucleation case, here large grain size and smoothness are not incompatible. That is, if adatom mobility on the substrate is sufficient, large 2D nuclei will form before the first monolayer coalesces, and then subsequent monolayers will grow epitaxially on those nuclei. But there is another problem. High adatom mobility requires a low surface diffusion activation energy, E_s , in accordance with **Figure 8**, but E_s tends to increase with the strength of the adsorption, E_d or E_c , as suggested in **Figure 7b**. At the same time, good

wetting requires low γ_i and therefore requires strong adsorption. As a result, it will not always be possible to achieve strong enough adsorption for wetting without immobilizing the adsorbate and preventing grain growth. Even so, small-diameter grains can become wider as the film grows thicker.

3.4 Texturing

The texturing described here refers to the crystal structure rather than the surface morphology, although they are often correlated. The degree of texturing is the degree to which the crystallites in a polycrystalline film are similarly oriented. In one limit, there is random orientation (no texturing), and in the other limit, there is the single crystal. A material in which the crystallites are nearly aligned in all three dimensions is called a “mosaic,” and the limit of a perfect mosaic is a single crystal. The degree of texturing is best measured by X-ray techniques. Texturing can occur in one, two, or three dimensions. Epitaxy is the best way to achieve perfect three-dimensional texturing. Epitaxy occurs when the bonds of the film crystal align with the bonds of the substrate surface, making the interfacial energy, γ_i , very low, zero in the case of homoepitaxy; this is when the film material is the same as the substrate material. In other cases, when there is no such arrangement to operate, the most common form of film texture is two-dimensional texture, in which the crystal plane is arranged relative to the rotation of two axes on the substrate plane. This means that the film has a preferred growth plane parallel to the substrate, but has a random orientation relative to the rotation of the axis (i.e., azimuth) perpendicular to the substrate plane. It is often desirable to deposit the film on a substrate that cannot be crystallographically aligned, such as an amorphous substrate (such as glass) or a substrate with crystal symmetry or lattice size very different from the film. In this case, it is very ideal to realize two-dimensional texture when the required film properties are also crystal anisotropy.

3.5 Submonolayer and lattice mismatch

Because of the importance of atomically abrupt interfaces, we will focus next on physical and chemical vapor deposition processes which operate far from equilibrium in the sense that $J_v \ll R_r$. This is achieved by reducing the deposition T , T_s , until J_v becomes negligible. It does not mean, however, that all of the steps in the deposition process are operating far from equilibrium. Recall from Section 3.2 that deposition is a series of steps: adsorption, surface diffusion, reaction, nucleation, structure development, and interdiffusion. To obtain good deposition rate control, it is only important that either the adsorption or the reaction step be far from equilibrium. To prevent the broadening of interfaces after they are formed, it is important also that T_s be low enough so that interdiffusion is negligible during the total time of structure deposition. However, if T_s is too low, surface diffusion will become negligible, and structural equilibration will not occur. This is the “quenched growth” regime, and the crystallographic quality of epilayers is poorer in this regime than at higher T_s . Fortunately, there is often a T_s “window” within which good crystallography and sharp interfaces can both be obtained. Much of the development work in epitaxy has involved modifying processes to widen this window.

In addition to non-equilibrium growth, one must also have chemical compatibility and reasonably good lattice match between layers to obtain good heteroepitaxy. Now let us move on to chemical interactions. Epitaxy is particularly sensitive to degradation by impurities and defects. Moreover, complete disruption of epitaxy can occur if even a fraction of a monolayer of disordered contaminant

exists on the substrate surface or accumulates on the film surface during deposition. This is because the depositing atoms need to sense the crystallographic order of the underlying material and chemical forces extend only one or two atomic distances. An island of surface contaminant becomes the nucleus for the growth of nonepitaxial material, and this region often spreads with further deposition, as shown in **Figure 12**, rather than being overgrown by the surrounding epilayer. Contamination can enter at any step in the thin film process. Removal of substrate contamination to improve adhesion is not discussed here. The additional substrate requirements that must be met to achieve epitaxy are of great concern. These include crystallographic order, submonolayer surface cleanliness, and chemical inertness toward the depositing species. Any crystallographic disorder at the substrate surface will be propagated into the depositing film. A few materials can be obtained as prepolished wafers with excellent surface crystallography. In other cases, careful preparation is necessary to remove the disorder introduced by wafer sawing and mechanical polishing. The crystallographic damage produced by polishing-grit abrasion extends into the crystal beneath the surface scratches, to a distance of many times the grit diameter, as shown by the dislocation line networks in **Figure 13a**. This damaged region must be removed by chemical etching. To promote uniform etching and prevent pitting, the “chemical polishing” technique is used. In this technique, the etchant is applied to a soft, porous, flat pad which is wiped across the wafer. If the depth of etching is insufficient, some damage will remain, as shown in **Figure 13b**, even though the surface may appear absolutely flat and smooth under careful scrutiny by Nomarski microscopy. However, these defects can be revealed by dipping the wafer in a “dislocation” etchant [13] that preferentially attacks them and thereby decorates the surface with identifying pits and lines. The crystallographic disorder at these defects, consisting of strained and broken bonds, raises the local free energy and thereby increases reactivity toward the etchant. After sufficient chemical polishing, the only remaining defects will be those grown into the bulk crystal, as shown at the etch pits in **Figure 13c**.

After crystallographic preparation of the substrate, surface contamination must be removed. In the final chemical cleaning step prior to wafer installation in the deposition chamber, one seeks to minimize residual surface contamination and also to select its composition so that it is more easily removed by the techniques available in the chamber.

Figure 12.
Effect of submonolayer surface contamination on epitaxy.

Figure 13.
Crystallographic damage due to wafer sawing and mechanical polishing.

Finally, the lattice mismatch is discussed. The expression of lattice mismatch factor is as follows:

$$f = \frac{(a_e - a_s)}{(a_e + a_s)/2} \approx (a_e - a_s)/a_s \tag{16}$$

Having now dealt with avoiding precipitates and controlling point defects, we can proceed to the problem of minimizing other crystallographic defects. It is useful to think of defects in terms of their dimensionality. Point defects are zero-dimensional (0D), while precipitates or disordered regions are 3D. Planar (2D) defects include grain boundaries, twin planes, stacking faults, and antiphase domain boundaries. Dislocations are line (1D) defects. We will see below how dislocations arise from the fractional lattice mismatch, f , at heteroepitaxial interfaces. For this purpose, we consider the simple square symmetry of cubic material growing in (001) orientation on a (001)-oriented substrate, although the same principles apply to other symmetries. **Figure 14** shows the various modes of

Figure 14.
Modes of accommodating epilayer lattice (solid circles) to substrate lattice (white circles).

mismatch accommodation. In the special case of perfect match (a), the lattices are naturally aligned, and the growth is therefore “commensurate” without requiring lattice strain. In (b–d), the atomic spacing of the epilayer, a_e , is larger than that of the substrate, a_s . In fact, f has been made quite large (0.14) here so that it may be readily observed, but it is much smaller in most heteroepitaxial systems of interest.

There are several ways in which lattice mismatch can be accommodated. In **Figure 14b**, bonding across the interface is weak, so that the epilayer “floats” on top of the substrate and is therefore “incommensurate” with it. This mode occurs, for example, with materials having a 2D, layered structure, such as graphite and MoS_2 [14]. In such compounds, there is no chemical bonding perpendicular to the hexagonally close-packed and tightly bonded basal plane, so that interaction of such a film with the substrate is only by Van der Waals forces. These weak forces are often strong enough to maintain rotational alignment with the substrate and to produce a small periodic compression and expansion in the epilayer lattice, but they are not strong enough to strain the epilayer so that it fits that of the substrate. There is a small periodic distortion in a_e as the lattices fall in and out of alignment periodically across the interface, and this produces a beautiful Moire pattern in STM images of the epilayer surface. Incommensurate growth can also occur when chemical bonding is weak because of a difference in bonding character between film and substrate. Chemical bonding can also be blocked by passivating the substrate surface.

In the more common situation, the epilayer is chemically bonded to the substrate, thus forming a unit called a “bicrystal.” A thin epilayer with small f is likely to become strained to fit the substrate in x as shown in **Figure 14c** and similarly in y . This is sometimes referred to as “pseudomorphic” growth, but it really is not, because no change in crystal structure has occurred. It is properly termed “commensurate growth” or “coherent epitaxy.” In **Figure 14c**, it is assumed that the substrate is much thicker than the epilayer, so that the substrate is rigid and all of the strain is in the epilayer. This “coherency” strain is then just $E_x = E_y = E_{x,y} = -f$, and the corresponding biaxial stress, σ_{xy} , is given by Eq. (18). The biaxial stress produces a strain in z , perpendicular to the growth plane, which is given by the three-dimensional form of Hooke’s law:

$$\varepsilon_z = \frac{1}{Y} (\sigma_z - \nu\sigma_x - \nu\sigma_y) = \frac{-2\nu\sigma_{x,y}}{Y} = \frac{-2\nu\varepsilon_{x,y}}{1 - \nu} \quad (17)$$

Here, the second equality was obtained by setting σ_z as it must be for the unconstrained direction, and the third was obtained using Eq. (18):

$$\varepsilon_x = \varepsilon_y = \varepsilon_{x,y} = \frac{(1 - \nu)}{Y} \sigma_{x,y} \frac{\sigma_{x,y}}{Y'} \quad (18)$$

(where Y' is sometimes known as the biaxial elastic modulus. Poisson’s ratio).

In **Figure 14c**, the epilayer is shown compressed in x and y and expanded in z in accordance with the above formula. This lattice is said to be “tetragonally” distorted, and the tetragonal strain is defined as:

$$\varepsilon_T = \varepsilon_z - \varepsilon_{x,y} = -\left(\frac{1 + \nu}{1 - \nu}\right) \varepsilon_{x,y} \quad (19)$$

X-ray diffraction measurement of the expanded atomic plane spacing a' in z can be used with Eq. (17) to determine the fraction by which the epilayer lattice has compressed to fit the substrate in x and y . Electron diffraction can be used only when the change in a is larger than a few percent, because the peaks are much broader than in X-ray diffraction. The strain energy stored per unit area in the

coherently strained epilayer U_e is obtained by integrating force over distance as the film is compressed toward a fit to the substrate, starting from the relaxed state shown in **Figure 14b**. The force to maintain the compression is supplied from the rigid substrate by bonding across the interface. The integration can be done in one direction and then doubled to account for the orthogonal direction. The force, F , in the x (or y) direction, per unit width of film in y (or x), is given by Eq. (20):

$$F_f = F_s \text{ or } \sigma_f h_f = \sigma_s h_s \text{ or } \left(\frac{Y}{1-\nu} \right)_f \epsilon_f h_f = \left(\frac{Y}{1-\nu} \right)_{fs} \epsilon_s \quad (20)$$

where $F_f, F_s; \sigma_f, \sigma_s$; and h_f, h_s are force, stress, and thickness of film and substrate, respectively, and the distance in x is the same as the strain E_x if we use a normalized film length of $L_x = 1$. Thus:

$$U_e \left(\frac{J}{m^2} \text{ or } \frac{N}{m} \right) = 2U_x = 2 \int_0^x F_x \frac{dx}{L_x} = 2 \int_0^{\epsilon_x} \left(\frac{Y}{1-\nu} \right) \epsilon_x h d\epsilon_x = \left(\frac{Y}{1-\nu} \right) \epsilon_x^2 h \quad (21)$$

The force of compression creates shear stresses in crystal planes that are not perpendicular to it, and along certain of these planes, the film will “slip” to relieve stress by breaking and then reforming bonds. After slippage, there will be extra rows of substrate atoms which are not bonded to the film, such as the one shown along y in **Figure 14d**. These features are known as misfit dislocations. Film stress is relieved by the development of a grid of such dislocations in the interface, the grid periodicity being determined by energy minimization, as we will see below. This growth mode is known as “discommensurate.” In addition to the bulk film strain energy, U_e , there is an interface energy, γ_i , as discussed in Section 3.3.1, but since it does not depend on h , it will be neglected below.

Usually, defects of any dimensionality (0D through 3D) are undesirable within a film unless they are introduced for a specific purpose such as doping. Films in electronic applications are particularly sensitive to degradation by defects. They disturb the lattice periodicity and thus locally alter the band structure of a semiconductor crystal, often producing charge carrier traps or charge recombination centers within the band gap. Defects of 1D and 2D also provide paths for electrical leakage and impurity diffusion. Thus, in heteroepitaxial growth, it is important to know what conditions have to be met to avoid the generation of misfit dislocations. This situation needs to be analyzed based on the discussion of the properties of dislocations. It is not discussed here because of the space.

4. Conclusion

The above discussion has examined the factors determining epitaxy film structure, topography, interfacial properties, and stress. The kinetic mechanism of atom adsorption, diffusion, reaction, nucleation, and texture is given. The kinetic characteristics and related technological conditions of two-dimensional nucleation and layered ordered growth are described. A new optimized denotation index (a T_s “window” within which good crystallography and sharp interfaces can both be obtained) for epitaxy growth is proposed. Much of the development work in epitaxy has involved modifying processes to widen this window. Finally, two main factors in epitaxial growth are proposed. Two principal factors are the degree of interaction of the depositing vapor with the substrate and with itself and the amount of energy input to the deposition surface. When the energy input is thermal, care must be taken to achieve good substrate T control.

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