Lecture Note #8 (Spring, 2020)

Application to Nanoscience

1. Stress and strain (7.1)
2. Types of interfaces (7.2)
3. Growth modes (7.4)
4. Nucleation theory (7.5)
5. Growth away from equilibrium (7.6)
6. Techniques for growing layers (7.7)
7. Nanotubes and nanowires (7.8)
8. Etching (7.9)

Reading: Kolasinski, ch.7

Growth and epitaxy (ch.7)
Stress and strain

-Stress & strain: mechanical properties of solids → crystal A + crystal B, interface, film growth, alloy particle, core-shell…

-The stress on the object is the applied force divided by the area to which it is applied (응력)
-Strain is the resulting distortion of the sample (변형, deformation)

-Field of the relations between stress and strain is called rheology

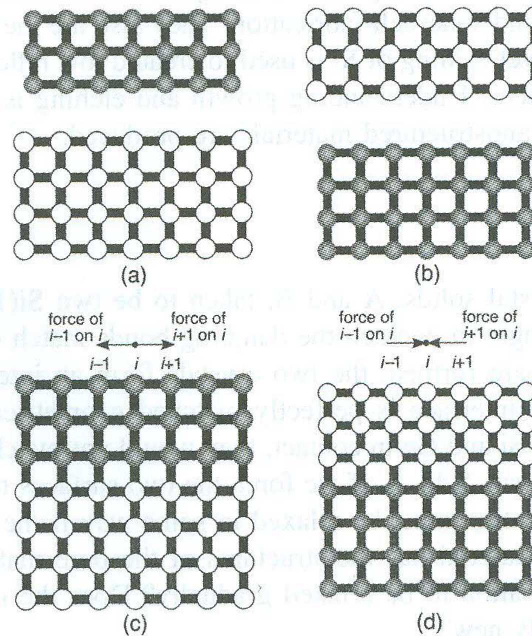
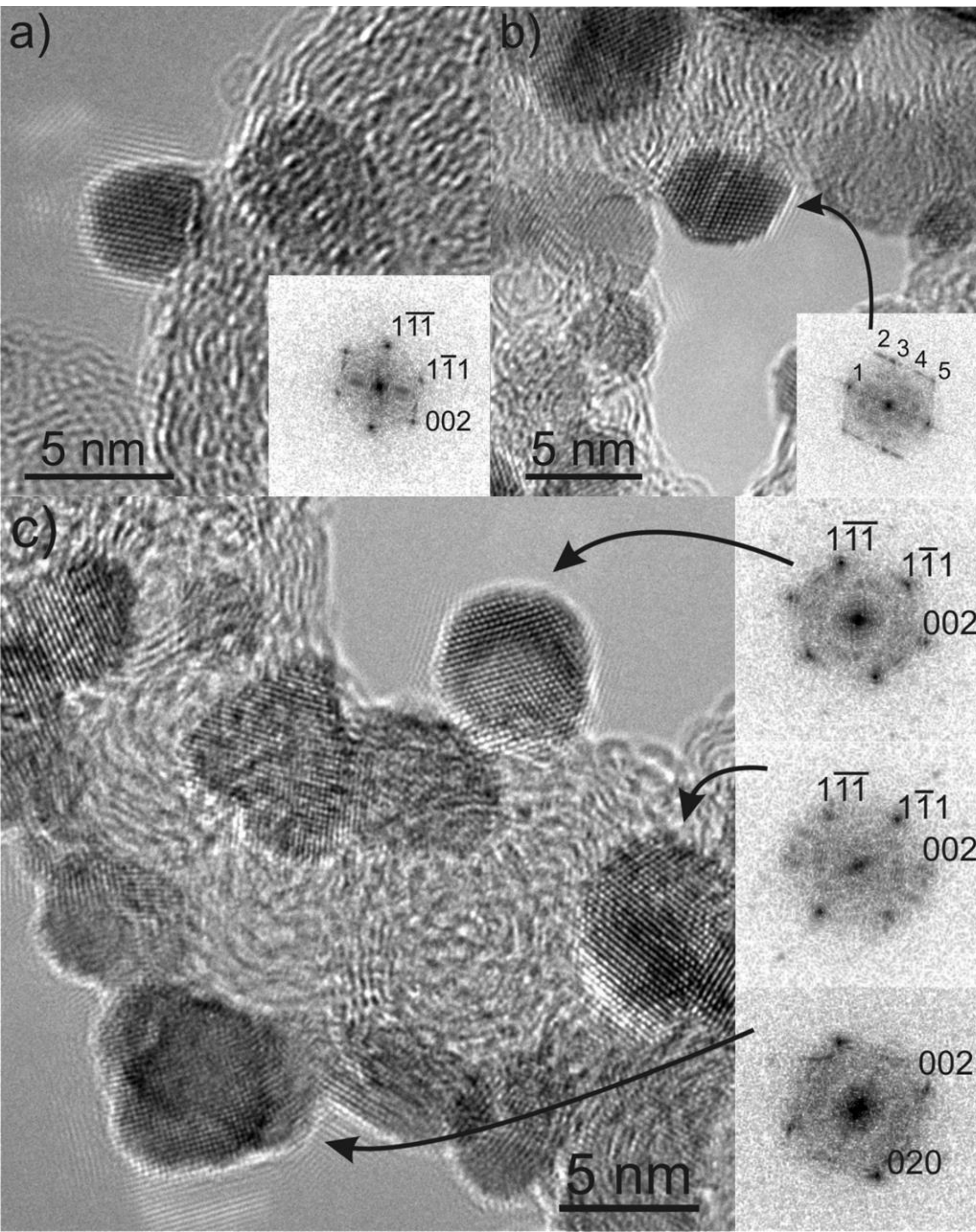


Figure 7.1 *Stress and strain in pseudomorphic layers in cross-sectional view. (a) Before attachment of the film to the substrate, the substrate has a larger lattice spacing than the film. (b) The film has a larger lattice spacing. (c) The film relaxes upon attachment, expanding to the lattice spacing of the substrate and is therefore under tension. (d) The film must contract upon attachment and is under compression. The forces along a line are as indicated. The net force vanishes in both cases but the directions of the components differ.*

Core-shell nanoparticles



Pd/C

Pt on Pd/C

Pt is epitaxially deposited onto Pd nanoparticles

Sung's group

-Stress & strain of interface (material A / Material B) or surface
(material A / adsorbate)

-Lattice misfit (or misfit strain), ε_0 is defined in terms of the lattice parameters of the overlayer a_l and the substrate a_s

$$\varepsilon_0 = \frac{a_1 - a_s}{a_s}.$$

For Ge overlayer on Si, $\varepsilon_0 = 0.042$, $In_xGa_{1-x}As$ on GaAs, $\varepsilon_0 = 0.0726x$

-the strain ε is defined by

$$\varepsilon = \frac{a_1 - a_s}{a_1} = \left(\frac{a_s}{a_1}\right)\varepsilon_0 = \frac{\varepsilon_0}{1 + \varepsilon_0}.$$

→ the layer is deformed compared to its natural lattice constant a_l

-Stress is a force per unit area as opposed to a force per unit length for surface stress
-Strain is a deformation
-The interfacial forces arising from stress lead to the deformations known as strained layers
-Strain depends both on the nature and magnitude of stress
-Tensil stress is positive, compressive stress is negative
-Strain at the interface of A and B depends on several factors
    relative sizes of the two materials (lattice constants)
    lattice symmetry of the two materials, e.g. hcp, diamond structure…
    relative strengths of A-A, A-B, B-B interactions
    temperature (thermal expansion coefficient)
    deposition conditions

Types of interfaces

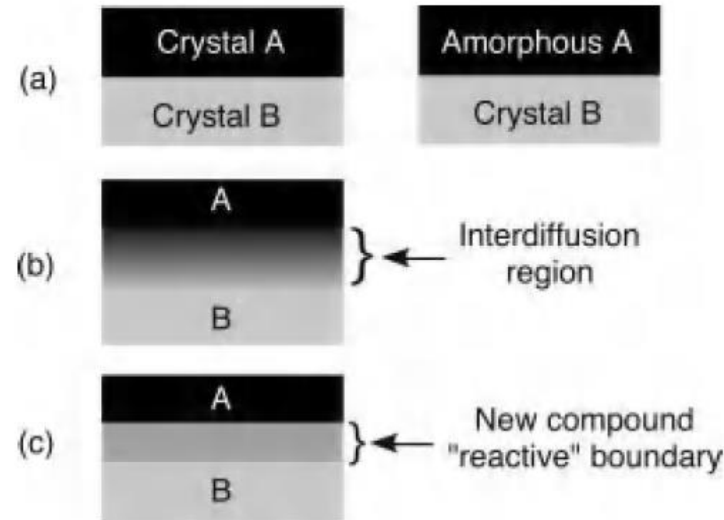


Figure 7.2 *The variety of interfaces that can be formed at the interface of two materials: (a) sharp interface; (b) non-abrupt interface; (c) reactive interface.*

Growth modes

-For liquid-on-solid growth, there are only two modes of growth: wetting (2D layer-by-layer) and non-wetting (3D island formation)
-For solid-on-solid growth, 3 growth modes → the appearance of strain → lattice mismatch

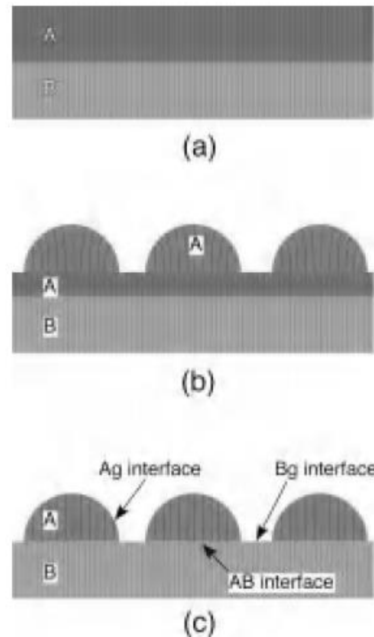


Figure 7.3 *Three modes of thermodynamically controlled growth of a solid overlayer A on solid substrate B in the presence of a gas (or, more generally, a fluid or vacuum) g. (a) Layer-by-layer growth (Frank-van der Merwe, FM) of two lattice matched ($\varepsilon_0 = 0$) materials. (b) Layer-plus-island growth (Stranski-Krastanov, SK). The strained wetting layer does not exhibit dislocations at either of its interfaces; however, the islands continuously relax with a lattice distortion in the growth direction. (c) Island growth (Volmer-Weber, VW) of lattice mismatched ($\varepsilon_o \neq 0$) materials with dislocations at the interface.*

- Metal on metal: epitaxial growth → most metallic adsorbates form ordered overlayer with a (1 x 1) surface structure on metal substrates
- Growth modes at metal surfaces: layer-by-layer fashion (Frank-van der Merwe mechanism), thin-film growth + 3D islands formation (Stranski-Krastanov mechanism), 3D islands form from the very beginning of metal deposition (Volmer-Weber mechanism)

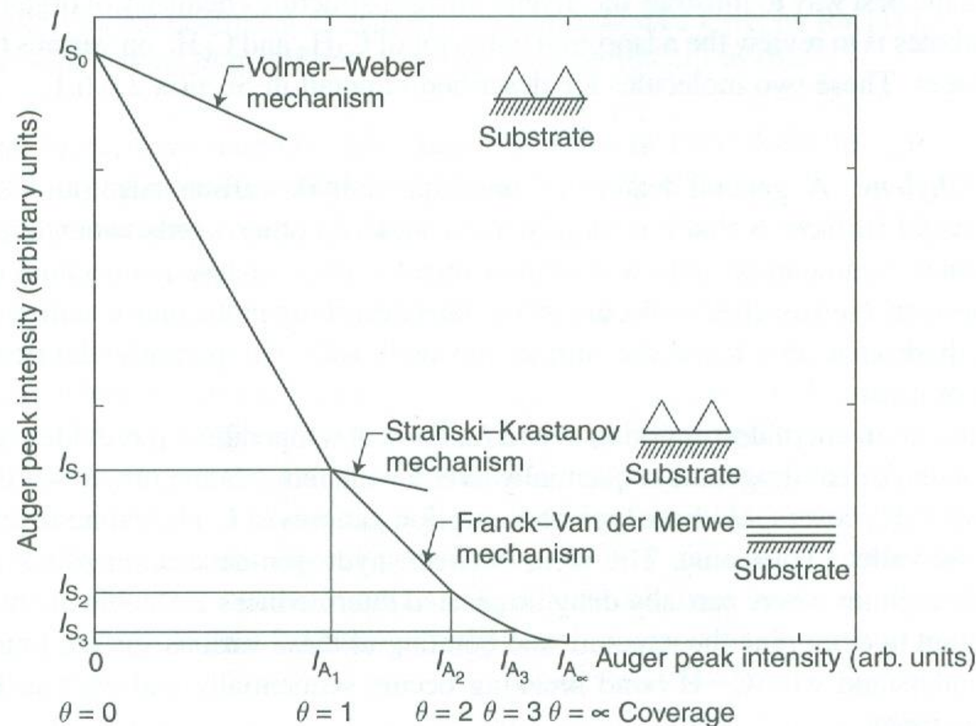


Figure 2.28. Growth of metal overlayers can occur in three different modes. Shown here is the behavior of the ratio of substrate and adsorbate Auger signals as a function of the deposition time for films that grow by the Volmer–Weber, Frank–van der Merwe, and Stranski–Krastanov types of mechanisms.

cf. structure of adsorbed monolayers

- Ordered monolayers on ordered surfaces due to mutual atomic interactions: in chemisorption, adsorbate-adsorbate forces are usually small compared to the adsorbate-substrate binding forces → adsorbate-adsorbate interactions between adsorbates dominate the long-range ordering of the overlayer
- Physical adsorption or physisorption: adsorbate-adsorbate interactions dominate adsorbate-substrate interactions → densest overlayer packing
- Metallic adsorbates: very close-packed overlayers because adsorbed metal atoms attract each other strongly → one monolayer “epitaxial growth” or multilayers, alloy formation by interdiffusion

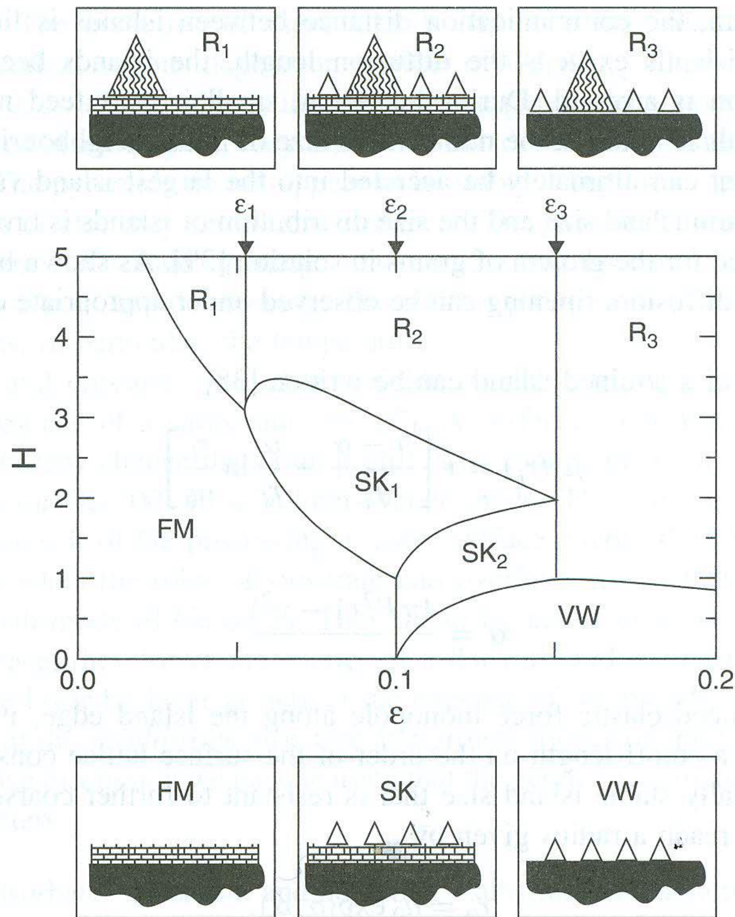


Figure 7.4 *Phase diagram calculated by Daruka and Barabási as a function of coverage H and misfit strain ε. The small panels at the top and bottom schematically represent the growth modes observed. The small empty islands indicate the presence of stable islands, while the large shaded ones refer to ripened islands. FM, Frank-van der Merwe growth; SK, Stranski-Krastanov growth (SK_1, wetting layer forms before islands; SK_2, wetting layer forms after islands); VW, Volmer-Weber growth. Ripening phases: R_1, Ostwald ripening in the presence of a wetting layer; R_2, a modified ripening phase with a wetting layer and small stable islands; R_3, a modified ripening phase with small stable islands but without a wetting layer. Reproduced from I. Daruka, A.-L. Barabási,* Phys. Rev. Lett., *79, 3708. © 1997 with permission from the American Physical Society.*

Oswald ripening

-Non-wetting adsorbate, water on H-terminated Si surface
→ Volmer-Weber growth (island formation)
→ water overlayer contracts into 3D islands
→ minimum energy is achieved when the contact area between the overlayer and the substrate is minimized
→ the surface area is minimized when one large island forms rather than any greater number of smaller islands (small islands are unstable with respect to larger islands)

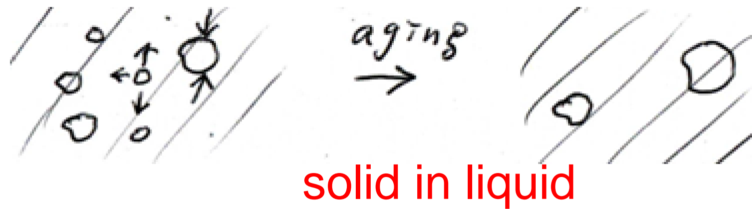
We now express what drives this result quantitatively. The chemical potential μ_i of an unstrained island of radius r_i can be written [38]

$$\mu_i(r_i) = \nu\sigma/r_i \quad (7.4.4)$$

where ν is the surface area per atom in the island and σ is the island edge (step) energy. In the absence of strain, Eq. (7.4.4) shows that the chemical potential of an island is inversely proportional to its radius. Therefore as expected, a thin film that does not wet a surface breaks up into a distribution of 3D islands. If the system evolves without constraint and in the absence of strain, coarsening of the initial layer/island distribution will tend to form one large island rather than any number of smaller islands.

Lecture Note #6

Oswald ripening



solid in liquid

desolution ↔ deposition process is in a dynamic equilibrium
to maintain a constant saturation solubility.

small particle → high solubility and large particle → low solubility

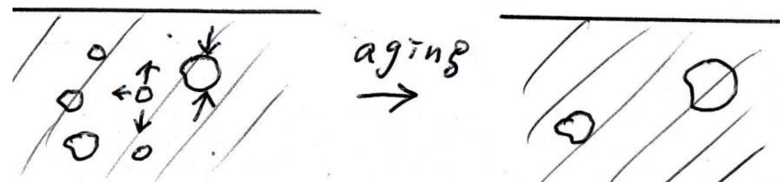
Large particles grow at the expense of the smaller particles → aging

minimize the total surface area → the way to reach a G_{min},
an equilibrium state

AgI sol → highly insoluble → little tendency of ripening (slow kinetics)

$CaCO_3$ sol → highly soluble → strong tendency of ripening (fast kinetics)

Sintering



solid in (on) solid

Nucleation theory

-The change in Gibbs energy upon forming a spherical cluster or droplet of radius r from N atoms (or molecules)

$$\Delta G = -N \ \Delta\mu + 4\pi r^2 \gamma \qquad (7.5.1)$$

→ chemical potential change brought about by the phase transformation of N atoms into a sphere with a surface energy given by the 2nd term

-Number of atom in the clusters and the radius are related by

$$N = \frac{4\pi}{3} \frac{r^3 N_A \rho}{M} = \frac{4\pi}{3} r^3 \overline{\rho}, \qquad (7.5.2)$$

where N_A is the Avogadro constant, ρ the mass density, M the molar mass, and $\overline{\rho}$ the number density.

-Combining (7.5.1) and (7.5.2) and differentiating with respect to either N or r → values for the size of critical classical nucleus

$$N_c = \frac{32\,\pi\gamma^3}{3\overline{\rho}^2 \Delta\mu^3} \quad \text{and} \quad r_c = \frac{2\gamma}{\overline{\rho}\Delta\mu}$$

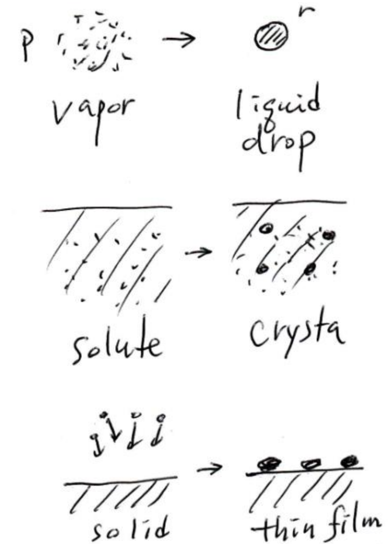
-Critical radius r_c → the smallest structure for which the probability of growth is greater than that of decay

-r_c →(7.5.1) → energy barrier to nucleation

$$\Delta_{max} G = \frac{4\pi r_c^2 \gamma}{3}$$

Formation of a new phase : nucleation and crystal growth

vapor → liquid drop
solute in a liquid → crystal



- In the initial stage of condensation a liquid drop of radius r is formed from a supersaturates vapor
- Small drop has a high vapor pressure → it tends to re-evaporate →
- Therefore, only droplets of a radius greater than a critical radius r_c (embryo) survive and grow.
- This process is called nucleation and the nuclei grow in time.

Consider the free energy change in nucleation of a droplet from a vapor.

nA (gas,P) → A_n (small liquid drop, r)

$$\Delta G = -nRT \ln(P/P_o) + 4\pi r^2 \gamma$$
$$= -(4/3)\pi r^3(\rho/M)RT \ln(P/P_o) + 4\pi r^2 \gamma$$

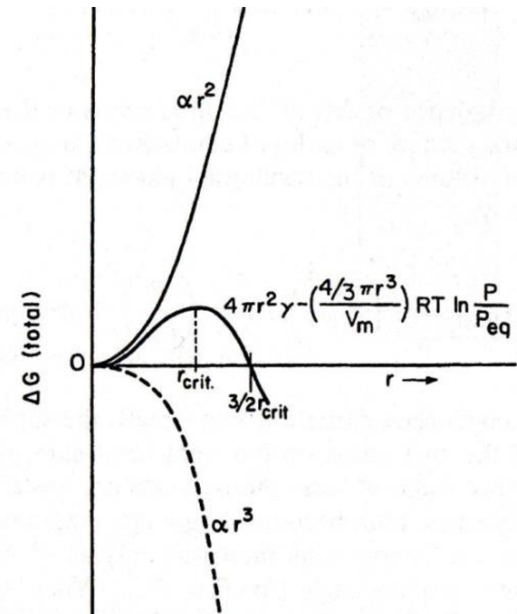
M= molecular weight, ρ = density
P_0 = equilibrium vapor pressure
P/P_0 = degree of supersaturation

$$d(\Delta G)/dr = 0 \text{ at } r = r_c$$
$$r_c = 2\gamma V_m / RT \ln(P/P_o)$$

This means there is always a free energy barrier of

$$\Delta G_m = 16 \pi \gamma^3 V_m /3 [RT \ln (P/P_0)]^2$$

which is overcome by thermal fluctuation.



* Related concepts

artificial raining: spraying dry ice particle in the damp air
seeding in crystallization: adding a crystal seeds in a supersaturated solution

Growth away from equilibrium

Thermodynamics vs. dynamics

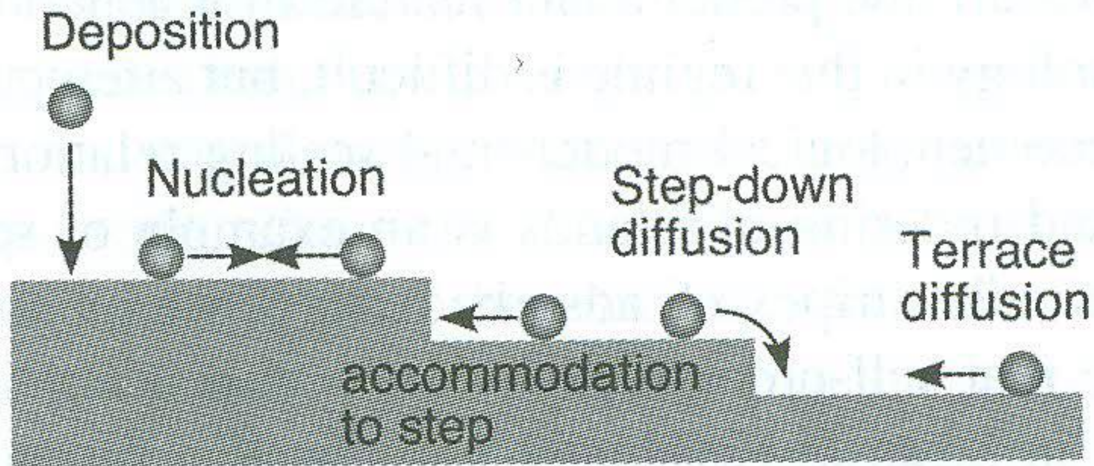


Figure 7.5 *Surface processes involved in film growth.*

Non-equilibrium growth modes

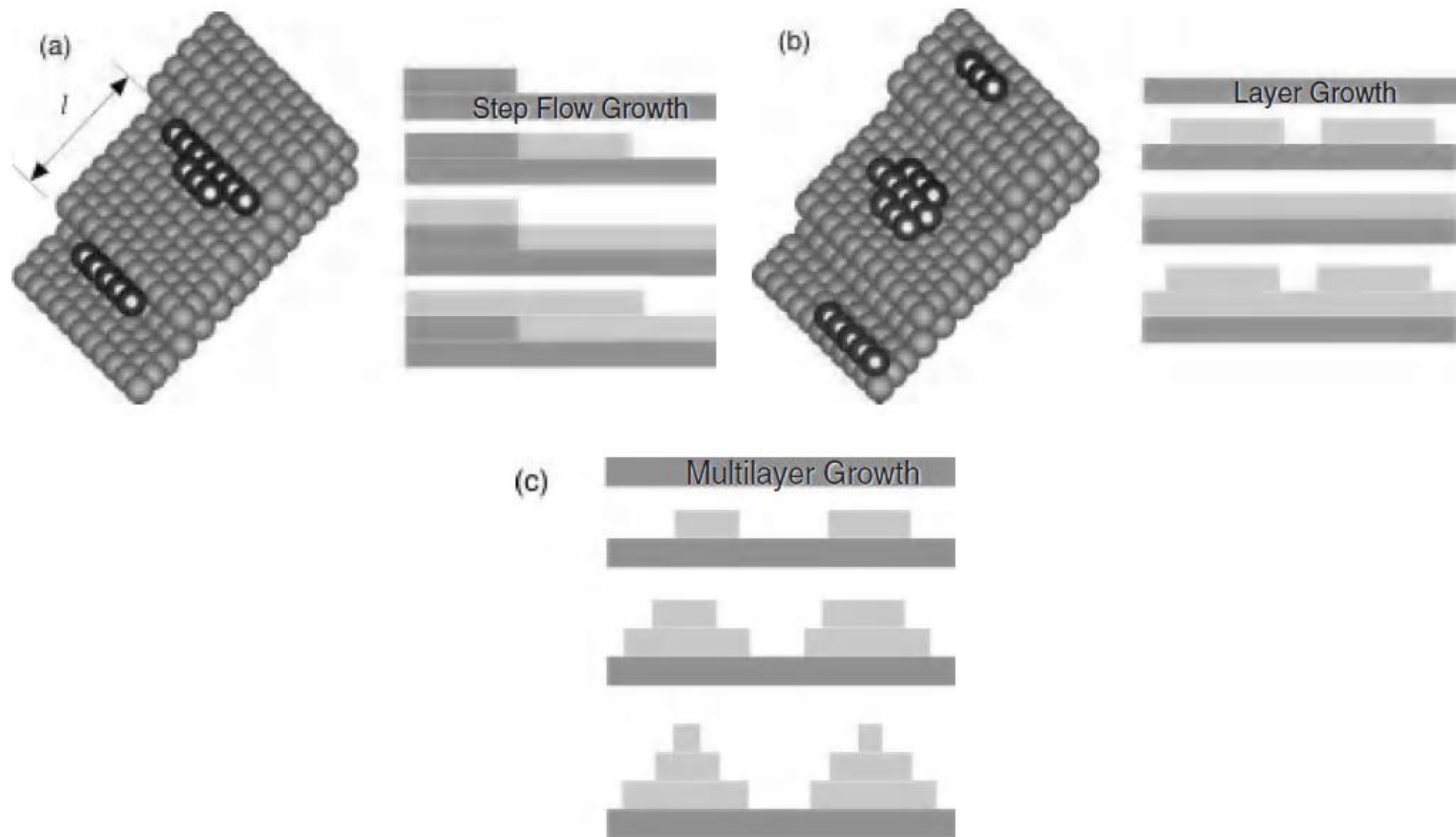
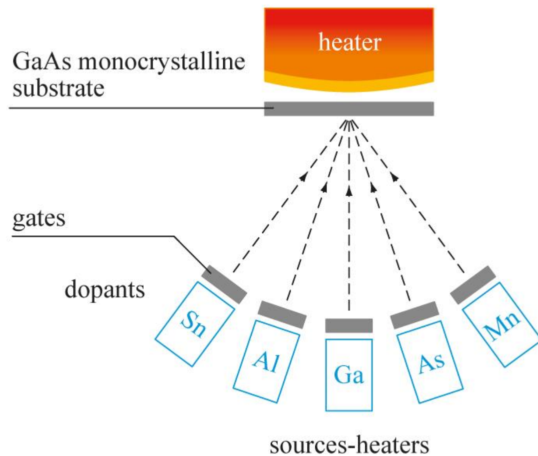
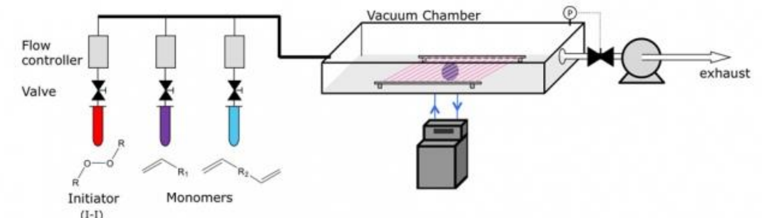


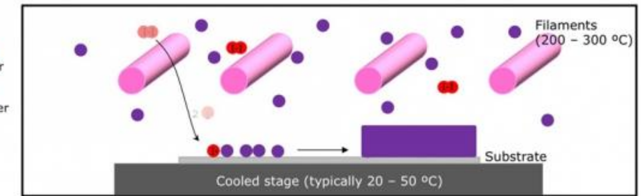
Figure 7.6 *Non-equilibrium growth modes: (a) step-flow growth; (b) layer growth by island coalescence; (c) multilayer growth.*

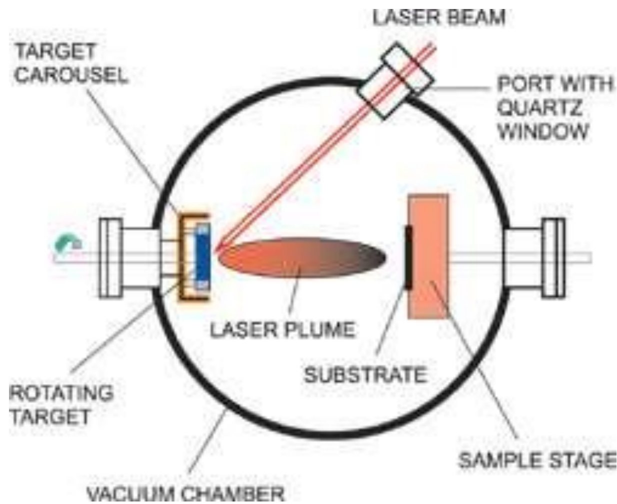
Techniques for growing layers

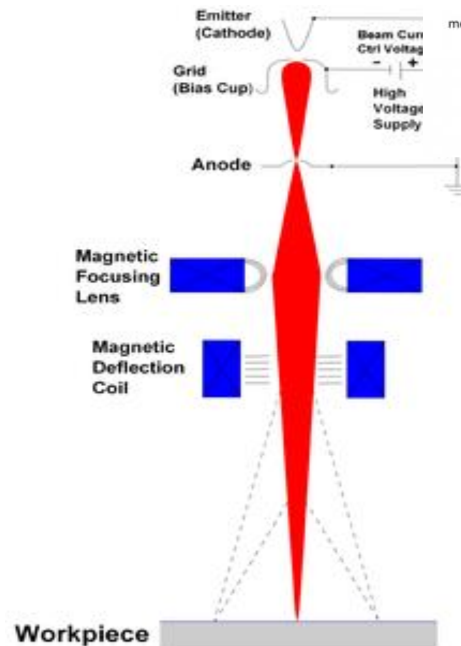
(1) Molecular beam epitaxy (MBE)
(2) Chemical vapor deposition (CVD)
(3) Ablation techniques: laser deposition, electron irradiation
(4) Physical vapor deposition: RF sputtering

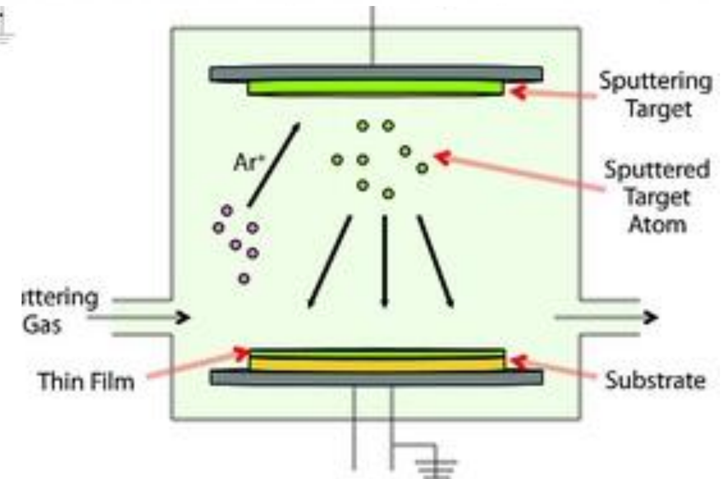












Nanotubes and nanowires

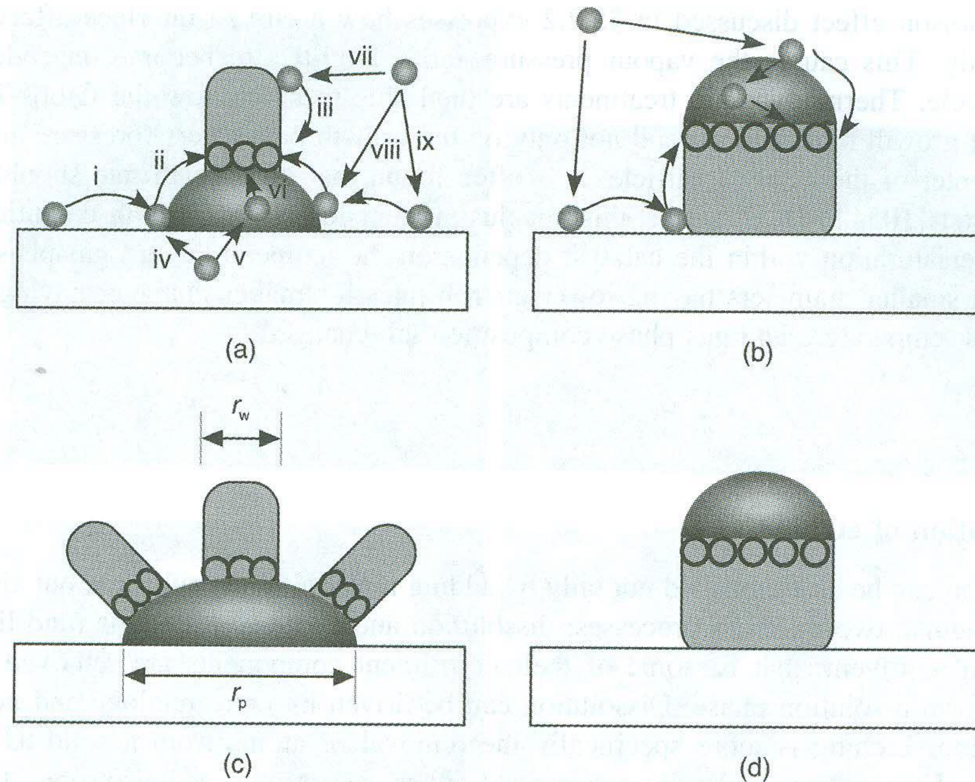


Figure 7.12 *The processes that occur during catalytic growth. (a) In root growth, the particle stays at the bottom of the nanowire. (b) In float growth, the particle remains at the top of the nanowire. (c) In multiple prong growth, more than one nanowire grows from one particle and the nanowires must necessarily have a smaller radius than the particle. (d) In single-prong growth, one nanowire corresponds to one particle. One of the surest signs of this mode is that the particle and nanowire have very similar radii. Reproduced from K. W. Kolasinski,* Curr. Opin. Solid State Mater. Sci. *10, 182. © 2006, with permission from Elsevier.*

Etching

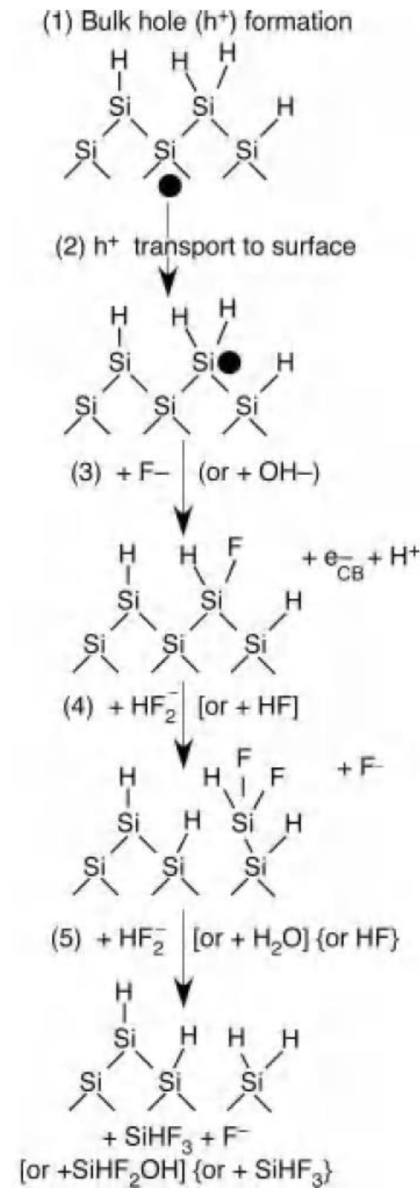


Figure 7.15 *The Gerischer mechanism of Si etching in fluoride solutions as proposed by Gerischer, Allongue and Costa-Kieling [171] modified by Kolasinski [172]. Electrochemical or photo-assisted etching is initiated by hole capture at the surface in a Si–Si back bond. This is followed by rapid replacement of H(a) by F(a), and slow addition of HF or* HF_2^-*. A final HF addition completes the etch cycle and leaves the surface H terminated.*

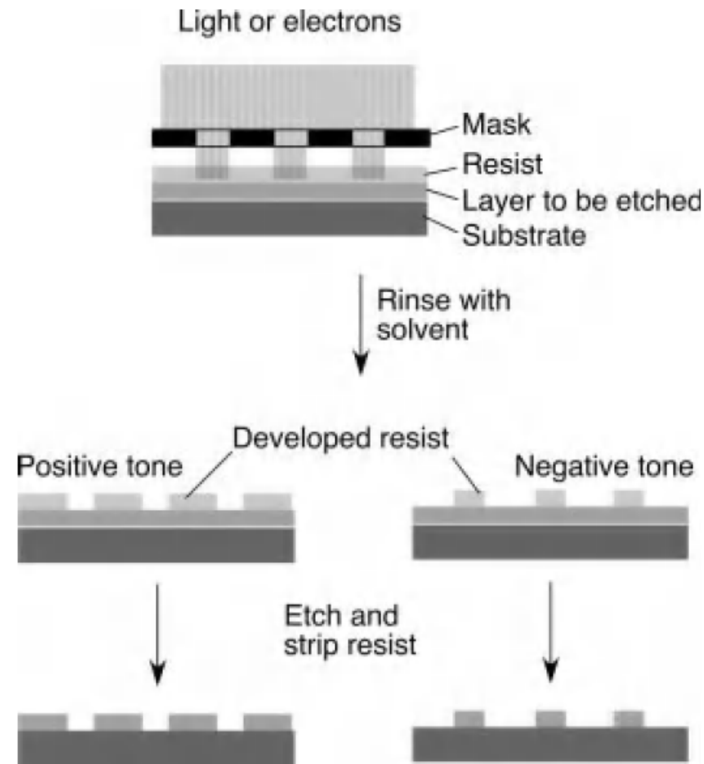


Figure 7.16 *A schematic illustration of the steps involved in lithographic pattern transfer. Irradiation through a mask transfers a pattern into the resist. Development removes the irradiated area of a positive tone resist, whereas the unirradiated region is removed from a negative tone resist. Etching transfers the pattern into the layer beneath the resist.*

Summary

- A stress applied to a lattice causes a deformation called strain.
- Strain relief is critical in the determination of interface structure. Heteroepitaxial layers often relax by the introduction of defects at the interface after they grow thicker than the critical thickness.
- The term surface tension should only be applied to liquids. For solids the proper term is surface energy.
- Surface energy can be thought of as being analogous to a two-dimensional pressure, compare Eqs (5.2.1) and (5.2.2), or else as the surface Gibbs energy, Eq. (5.2.4).
- The multilayer growth of an adsorbate on a substrate is characterized by one of three growth modes: Frank-van der Merwe (layer-by-layer), Stranski-Krastanov (layer + island) or Volmer-Weber (island).
- At equilibrium the growth mode is determined by the effects of strain and the relative strength of the A–A, A–B and B–B interactions (A = adsorbate atom and B = substrate atom).
- Under non-equilibrium conditions the dynamics of adsorption, desorption and diffusion can lead to deviations from the equilibrium growth mode (kinetically controlled growth).
- Self-limiting chemistry is used to grow layers with atomic composition and thickness control.
- Etching involves reactions that consume the surface.
- Anisotropy (with regard to crystallography and surface site) in the etch process can lead to a range of final structures ranging from sharp tips to smooth surfaces to porous solids.
- The region of the surface that is etched can be controlled by the use of a mask.
- In a positive tone resist, the exposed portion of the resist is removed during development, whereas in a negative resist the unexposed region is removed.