13

Surfaces, Nanoparticles, and Foams

CHAPTER PREVIEW

This chapter is the first of a three-part series on interfaces. We are dividing the discussion only to make it manageable. An interface is a planar region separating two domains or materials. Hence, we have the definition of a surface as the region that separates a solid or liquid from gas or vacuum. The reason for using the word "region" is to make it clear from the beginning that the surface has a thickness; it is not the mathematical definition. Powder processing is the traditional route for forming ceramics; in powders the ratio of surface area to volume is large. With nanoparticle powders, the ratio can be huge.

We first discuss two important questions concerning surfaces.

- What do we mean by the word surface?
- Why are surfaces so important for ceramics?

We then consider, from several viewpoints, the two most important properties of surfaces.

- The energy associated with a curved surface is greater than that for a flat surface.
- We add material to the bulk solid by attaching it to the surface.

As always, we keep in mind the question: what is special about ceramics?

13.1 BACKGROUND TO SURFACES

A surface is just the interface between a solid (or liquid) and a gas or vacuum. In general, the surface of a material, or any interface between materials, is a region of excess energy relative to the bulk or matrix. To maintain the lowest total energy for the system, the configuration of the surface adapts itself to minimize this excess energy. Impurities or dopants that lower the surface energy tend to concentrate in the surface. Similarly, such *defects* move to the interface if by segregating there they lower the overall energy of the system even if it raises the interfacial energy. The surface tends to orient parallel to certain crystallographic planes that have a lower energy.

The surface energy can be intentionally lowered using a wetting agent or a (liquid or solid) surfactant. For example, the interfacial energy of liquid Ni in contact with Al_2O_3 can be changed by the presence of Ti at the surface. The Ti is strongly attracted to the oxide interface because of its high chemical reactivity with oxygen. This type of interaction is so common that a major problem in studying ceramic surfaces is to know if the surface is clean. During all ceramic processing we can assume that the surface is not perfectly clean.

Throughout our discussion of ceramic surfaces, we are concerned with four interrelated concepts: energy, formation, movement, charge. As usual, only the final one, charge, is particular to ceramics.

- The *energy* of an surface depends on many factors, including the material and structure (crystalline or not) and, if crystalline, the crystallography and plane. We discuss how to measure this parameter.
- *Formation* occurs only if it is energetically favorable. We need to discuss the relevance of Wulff plots to understand surfaces.
- *Movement* can occur if it does not increase the total energy or if it minimizes this increase.
- *Charge* distribution, and thus the bonding, is different at a surface. Charge must influence the value of the surface energy, but it is almost an unknown factor.

Many features of surfaces, and interfaces in general, are similar in all materials.

- A pressure difference is always present across a curved surface (thermodynamics).

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- The structure of surfaces can relax from the bulk-terminated configuration (physics).
- Surfaces can be wetted with a thin layer of impurity or a second phase (energetics).
- The ionicity or covalency and crystallography can affect surfaces (chemistry).

Surfaces and their interaction with impurities and particles are being extensively modeled using the computer. Some researchers might say that computer modeling may be the only method for studying clean surfaces.

13.2 CERAMIC SURFACES

The surface is particularly important for ceramics because we are often using powders at some stage of processing: the surface area-to-volume ratio is larger for powders than for bulk materials. Many uses of ceramics rely on their inertness or reactivity, but nanoparticles of "inert" ceramics can be very reactive, partly because of this enhanced ratio. Failure of a ceramic usually occurs first at the surface. Catalysis is enabled at the surface. Sintering, perhaps the most important processing route for ceramic materials, is the process of joining two surfaces together. Remember during this discussion that in the thermodynamic analysis of surfaces, surface energy and surface tension are properties of the continuum. Surface tension is usually assumed to be synonymous with surface energy, but this is not necessarily so. We must consider how we relate these continuum parameters to the atomic structure.

- Surface steps: when we need to consider the atomistics. Special surface sites influence the energy of surfaces.
- Composition: is the surface clean? If it is clean, does it have the bulk-terminated structure, or has it relaxed?

What is special about surfaces of ceramics? We have to think about surface structure, otherwise we won't appreciate what is special.

- The charge and covalent bonds: charge cannot necessarily be redistributed.
- Surface energy tends to be much more dependent on the plane in ceramics.
- These two points are probably not independent.

Because the properties of interfaces vary so much, the morphology of interfaces in real ceramics may be unusual. Therefore, to answer what is special, we need to summarize the features that are common to all materials first. Then we can ask: what is different in comparison to metals? Ionic materials and covalent materials (e.g., Si, Ge, GaAs) both have local charge variations. The directional bonding of the covalent materials means that they can have "unsatisfied" bonds; they are known as dangling bonds. (We have encountered them before when discussing point defects).

SURFACES OF MINERALS

Interactions of minerals with the environment are important in decreasing contamination and waste management. This is sometimes referred to as the field of environmental mineralogy. Topics include microbial interactions with minerals, anthropogenic influences, contaminated land and waste management.

13.3 SURFACE ENERGY

Surface energy is clearly a very important quantity. It is almost never well known if it is *known* at all. There are two important questions that we need to answer about surface energy.

- How do we define the energy of a surface?
- What factors determine the surface energy?

Definition. The easiest way to define surface energy is to start with a liquid (it could, for example, be a molten ceramic) and imagine that it is suspended in a wire frame. One bar of the frame is movable and allows us to increase the surface area by an amount dA. The force that we have to apply must be sufficient to overcome the opposing surface tension, γ. The work done, dw, in increasing the surface area is

$$dw = -\gamma dA \tag{13.1}$$

The term "tension" is a little confusing when we consider solids because it implies that there is an associated stress. With our example of a liquid in a metal frame, we are actually stretching the surface, and the atoms in the liquid are moving from the bulk to the surface to increase the surface area. We could not imagine doing the same thing with a solid except maybe close to the melting temperature. In solids, we regard γ as the energy required to form the surface. It is important to note that the surface energy is not usually equal to the surface stress—the work required to deform the surface—though we often assume it is. For a liquid they are equal.

From the combined statement of the first and second laws of thermodynamics, we can write that the change in internal energy, dE, is:

$$dE = TdS - PdV + \gamma dA + \sum \mu_i dn_i \tag{13.2}$$

TABLE 13.1 Surface Energies of Various Materials in Vacuum or Inert Atmospheres

Material		*Temperature (°C)*	*Energy (mJ/m²)*
Water	Liquid	26	72
Cu	Liquid	1,120	1,270
Ag	Liquid	1,000	920
Alumina	Liquid	2,080	700
Cu	Solid	1,080	1,430
Ag	Solid	750	1,140
Alumina	Solid	1,850	905
(100) NaCl	Solid	25	300
MgO	Solid	25	1,000

We can then define the surface energy as:

$$\gamma = \left(\frac{\partial E}{\partial A}\right)_{S,V,n_i} \tag{13.3}$$

A similar expression involving the Gibbs free energy can be written:

$$dG = -SdT + VdP + \gamma dA + \sum \mu_i dn_i \tag{13.4a}$$

The surface energy is written as:

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{P,T,n_i} \tag{13.4b}$$

Some examples of surface energies are given in Table 13.1. The range of values is quite large. Even if we compare only the values for solids, you can see that, for NaCl, $\gamma = 300$ mJ/m^2; it is three times greater for MgO (think about the charge). As a general rule, the surface energy decreases as the temperature increases (Eötvos rule). The surface energy of a liquid is lower than that of the corresponding solid. For example, we can compare values for Al_2O_3:

- Al_2O_3 (solid) $\gamma = 905$ mJ/m^2
- Al_2O_3 (liquid) $\gamma = 700$ mJ/m^2

In general, you should be very wary when given precise values for surface energies.

13.3.1 Approximation of Surface Energies

The surface energy of a solid depends on the crystal structure and orientation and can be estimated by a simple calculation. First, we assume that the binding energy of an atom is the result of bonds to its nearest neighbors. The energy, ε, of one bond is then

$$\varepsilon = \frac{\Delta H_s}{0.5 Z N_A} \tag{13.5}$$

ΔH_s is the molar enthalpy of sublimation (the energy to break all the bonds), Z is the coordination number, and N_A is the Avogadro number.

The work, w, required to form a surface— for example, if we cleave a crystal—is going to depend on the number of bonds, x, per atom that we break (so x depends on the cleavage plane).

$$w = \frac{x}{2}\varepsilon = \frac{x\Delta H_s}{Z N_A} \tag{13.6}$$

The surface energy, γ, is then

$$\gamma = \frac{x\Delta H_s}{Z N_A}\left(\frac{N}{A}\right) \tag{13.7}$$

The term (N/A) is the number of atoms per unit surface area. You can see from Table 13.1 that this approach gives only a very approximate (but not unreasonable) result, although it looks very precise. The reason is that second-nearest neighbors are not considered in the calculation (these are of course extremely important in ionic crystals), and it is also assumed that the strengths of the remaining surface bonds are the same as the bulk values. The calculation also does not consider charge—an important consideration for ionic ceramics! Estimated values for metals compare much more closely to the experimental values. (The calculation for Cu, for example, is given by Ragone 1995). What calculations using equation 13.7 do show us is that γ varies with crystal structure and surface orientation. The practical application of these differences is evident when we try to etch materials using acids. Different planes etch at different rates.

The chemical etch rates for Ge on the (100), (110), and (111) planes are 1.00, 0.89, and 0.62, respectively.

The implication is that the (100) plane of Ge has a higher energy than either (110) or (111) planes. The importance is that often when we try to etch a semiconductor we want to produce a smooth surface rather than a faceted one—unless we want to make V-MOS devices.

CALCULATING A SURFACE ENERGY

We can estimate the value of γ for the (100) face of NaCl. Take $x = 1$.

$\Delta H_s = 235{,}000$ J/mol (value for NaCl from Kubaschewski and Alcock 1979).

For NaCl, $Z = 6$.

$$N_A = 6.022 \times 10^{23}\ \text{mol}^{-1}$$
$$(N/A) = 1.26 \times 10^{19}\ \text{m}^{-2}$$
$$(a_{NaCl} = 0.5640\ \text{nm})$$

Giving $\gamma = 0.82$ J/m^2

13.3.2 Effect of Structure and Orientation

The surface energy, γ, depends on the structure, which depends on the orientation. We have developed two approaches for considering this orientation dependence: the Wulff plot and the inverse Wulff plot.

- The *Wulff plot* draws a graph of γ versus θ. This construction was developed to allow the equilibrium shape of crystals to be determined when the surface energy depends on crystallography.
- The *inverse Wulff plot* shows $1/\gamma$ as a function of θ.

The Wulff plot is the conventional plot for surfaces. An example of such a plot is shown in Figure 13.1. The most important point is that you have cusps in γ versus θ. In ceramics, this certainly occurs; if the energy were isotropic, the Wulff plot would be a circle. What is not certain is how many cusps you have. Note that such γ versus θ plots do not take into account the orientation of the surface plane; that is, having fixed σ, you must still fix $\mathbf{n}$, the surface normal.

Experimentally, we can determine the equilibrium shapes of crystals by annealing small single-crystal particles at high temperature in an inert atmosphere or by annealing small voids (inverse particles) in a crystal. Figure 13.2 shows an example of a bulk UO_2 sample that has been heat-treated so that the pores achieved a near-equilibrium. The length of the facets in the small void can be used to determine the relative energies of the (100) and (110) planes.

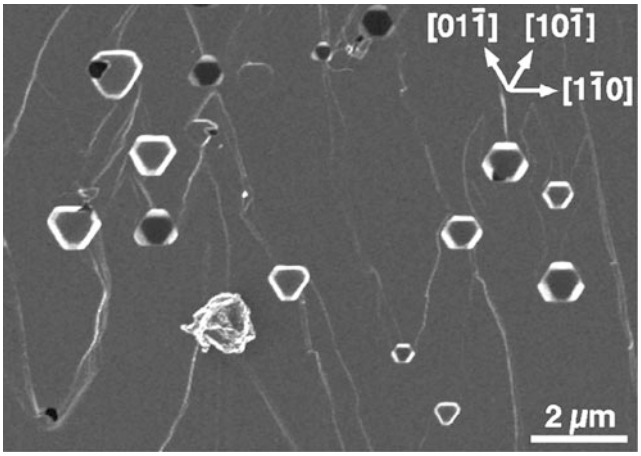

FIGURE 13.2. Faceting of small voids in UO_2.

13.4 SURFACE STRUCTURE

We illustrate some special surfaces using a series of figures. In continuum models of surfaces, the surface is a smooth curve; at the atomic level, it is always faceted. A terminology for the different surfaces is summarized in Figure 13.3. The surface can form large flat facets (F) that are really facets on two planes separated by a ridge (S) and surfaces that are not atomically smooth at all (K). Beware of the bias that carries over from metals, such as the picture that crystals are built by stacking cubes or that all ions are hard spheres. Ions can relax into the surface (relative to their bulk positions), and this relaxation depends on the crystallography of the surface. The relaxations are also different at steps on the surface.

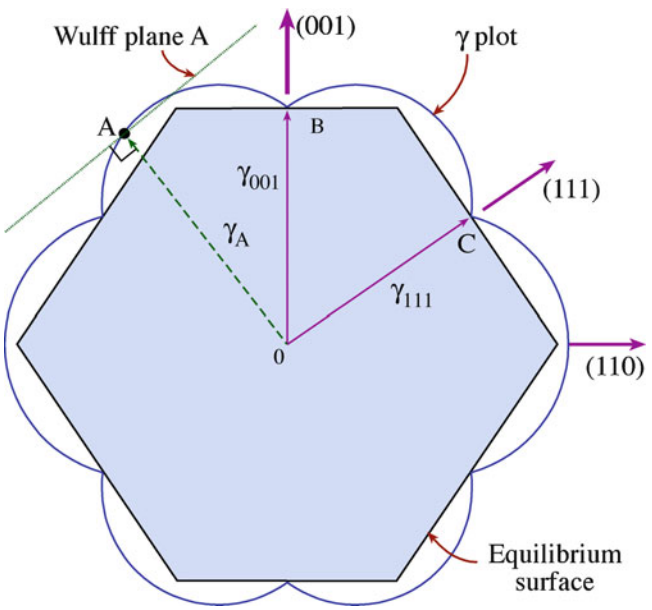

FIGURE 13.1. Wulff plot looking along the [1$\bar{1}$0] direction for a face-centered cubic (fcc) crystal.

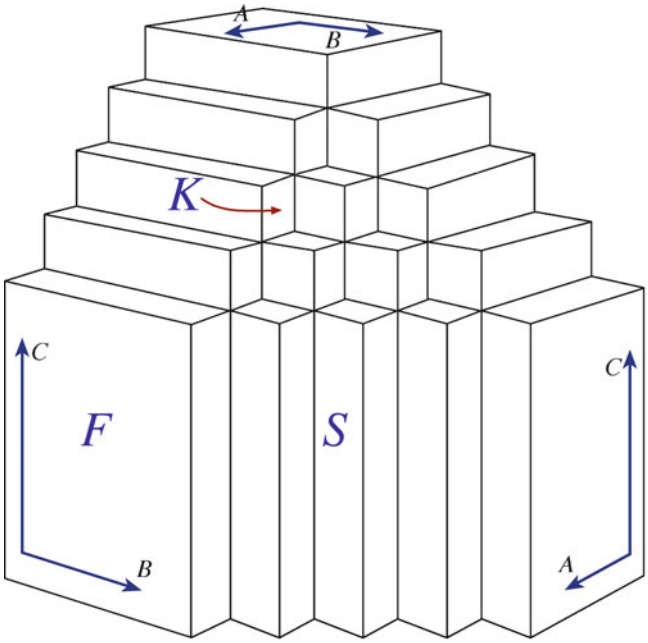

FIGURE 13.3. Terminology for facets, steps, and kinks on surfaces.

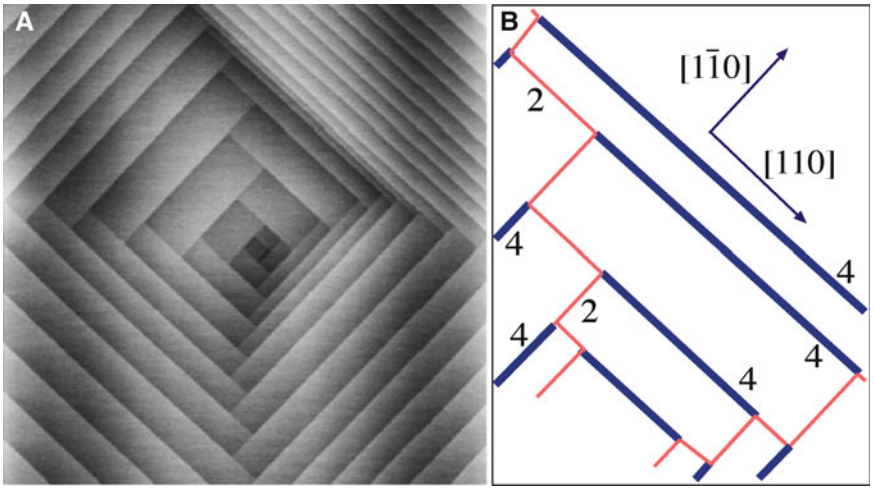

FIGURE 13.4. Faceted shallow thermal etch pit on the (001) surface of spinel. Numbers 2 and 4 refer to the height of the steps (0.2 and 0.4 nm, respectively).

Flat surfaces. The surface of a spinel crystal with an emerging dislocation is shown in Figure 13.4. The reason for choosing this figure is that it shows a ceramic surface that is atomically flat parallel to the step in this figure, for a distance over 10 μm. Step heights can be multiples of a unit value. When the unit cell is large, the definition of an atomically flat surface is less clear. For example, the surface of a zeolite is important in processing, but the surface and near-surface pores are connected: the surface area is much greater than the geometric area of the surface. (Remember the idea of the Mobius strip!)

Rumpled surfaces. The term *rumpled* refers to the local undulations on the surface. The rumpled surface is *crystallographically* flat, but local displacement of the ions means that it is not *geometrically* flat. The difference between relaxation and rumpling is that relaxation refers to the average change in the spacing of the plane nearest to the surface and the second plane when compared to the bulk value. Rumpling, on the other hand, refers to the displacement of the cation layer relative to the anion layer in a direction normal to the surface.

If an initially flat surface is not in its lowest-energy configuration, it *facets* when heated to a high enough temperature. You can envision how this process can occur by considering Figure 13.5. The surface is initially flat; if no extra material is added, a trench must form if a ridge forms. Facet growth thus involves surface diffusion normal to the *geometric* surface.

We might say that the surfaces of *nanoparticles* are their most important feature because they determine all of their properties. As is clear from Figure 13.6, the facet junctions on nanoparticles are also much more prominent.

The *chemistry* of surfaces can be very different from the bulk material. Clearly, the bonding is different on the surface. On oxides, in particular, OH groups may be present even if you think the environment is dry. Detecting hydrogen in or on a material is tricky. Such hydrated surfaces behave differently, and the surface energy can differ from that of the dry surface.

A VERY IMPORTANT BUT SIMPLE CALCULATION

The pressure in the void must do work to change the surface area. The equilibrium condition is then given by the energy balance.

$$\Delta P dv \ + \gamma dA = 0$$

For simplicity, assume that the void is a sphere (in using one value for γ, we've already assumed that the energy is isotropic). We know dv and dA in terms of r.

$$dv = 4\pi r^2 dr$$

$$dA = 8\pi r dr$$

Combining these three equations gives

$$\Delta P = \gamma \frac{8\pi r}{4\pi r^2}\left(\frac{dr}{dr}\right) = \gamma \frac{2}{r} = \frac{2\gamma}{r}$$

A surface will have two principal curvatures, r_1 and r_2 (which can either be positive or negative); we write

$$\Delta P = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

One special feature of ceramic surfaces is the result of covalent and ionic bonding. Ceramics have charges and charge dipoles. These charges are often uncompensated at the surface, at least on the short range, as illustrated in Figure 13.7.

13.5 CURVED SURFACES AND PRESSURE

The idea for curved surfaces and pressure is the same as we discussed for the bowed dislocation but we've added a dimension. If we reduce the area of the surface, we lower

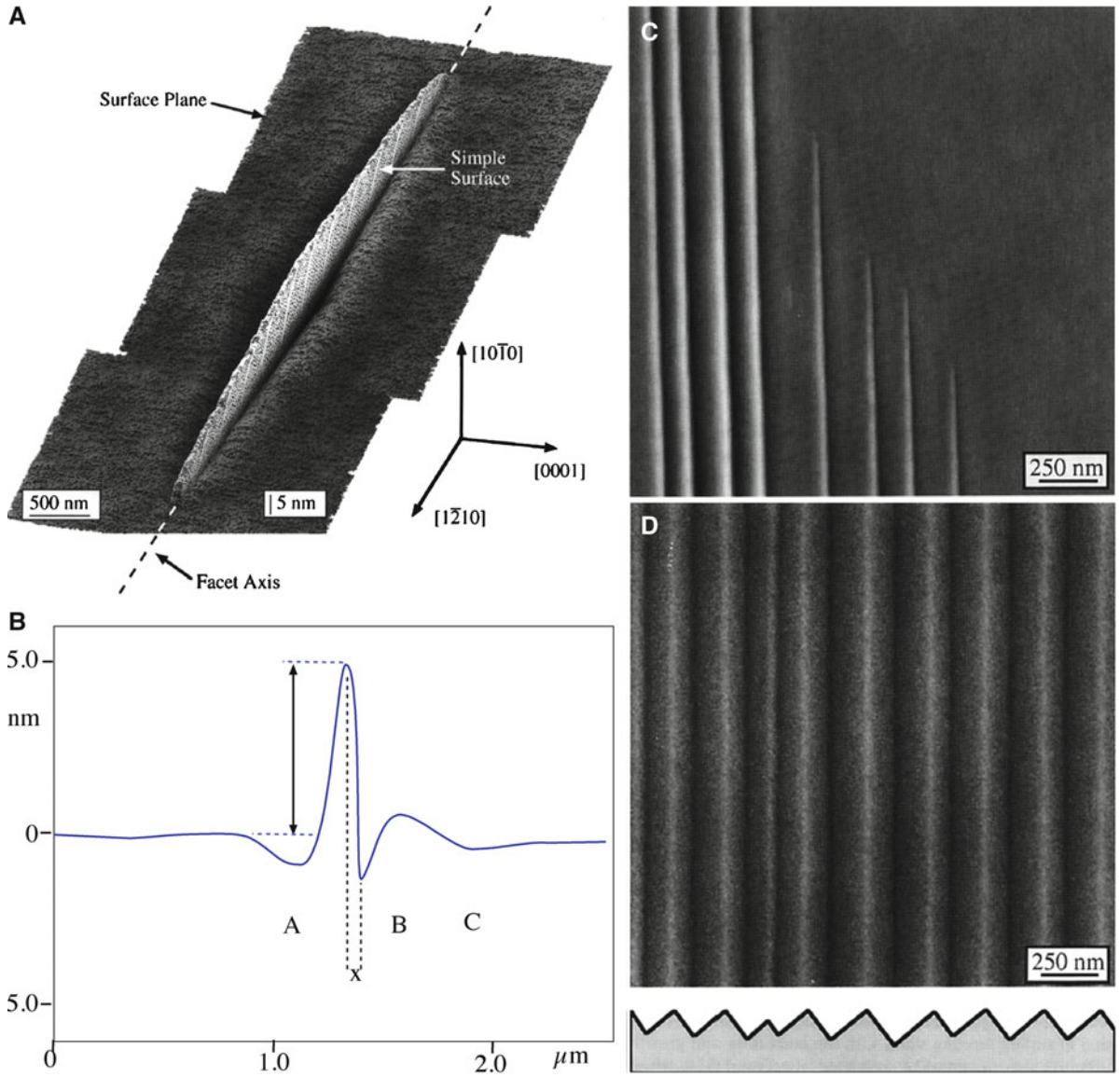

FIGURE 13.5. Initiation of faceting on the m-plane of sapphire.

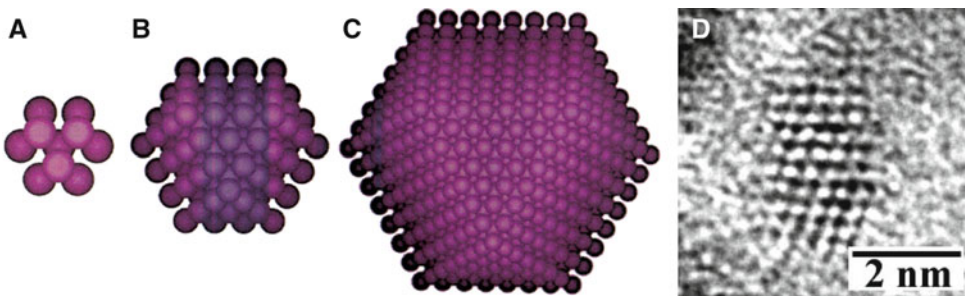

FIGURE 13.6. Fraction of atoms sitting at the surface of a nanoparticle. (A) There are 10 atoms, all on the surface. (B) There are 92 atoms, with 74 on surfaces (80%). (C) There are 792 atoms, with 394 on the surface (50%). (D) High-resolution transmission electron microscopy (HRTEM) image of a faceted nanoparticle of CdSe.

the energy. Hence, if a surface is curved, we can imagine that there is a force that wants to reduce the area of the surface: the force acts on an area of the surface; and the force divided by area is the pressure. Picture how you can take a small ring, fill it with a soap film and blow a bubble. The pressure is provided by the air: if you stop blowing, the surface becomes flat again. The analogy is quite close except that the surface energy of the soap film is isotropic (and there are actually two surfaces).

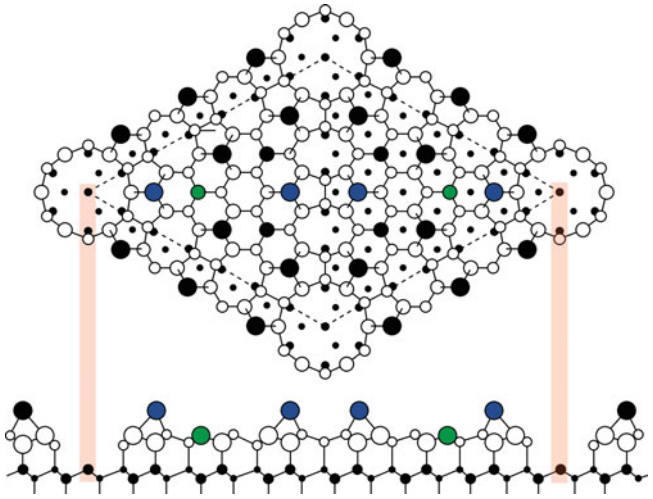

FIGURE 13.7. Relating dangling bonds to the 7 × 7 reconstruction of the {111} Si surface.

TABLE 13.2 Pressure Due to Surface Curvature for Silica Glass (1,700°C; $\gamma = 300$ mJ/m^2)

Sphere diameter (μm)	ΔP MPa	$\frac{P}{P_0}$
0.1	12	1.02
1.0	1.20	1.002
10.0	0.12	1.0002

There is also a torque term in the surface tension, just as there is for curved dislocations, but this term is usually ignored. To make this force more physical to us, we regard this surface energy as a surface tension. The pressure difference across a curved interface is real and occurs in all materials. In small gas-filled voids created by implanting Xe into MgO (or Si or Al), the Xe is crystalline if the void is small enough because the internal pressure is so high. The Xe can interact with other defects just like any small crystal inside a crystalline matrix, unless the defect is a crack! A simple example is calculated in Table 13.2.

The concept of pressure due to surface curvature is very important in ceramics because we often encounter very curved surfaces (e.g., at small grains, voids, or particles, which are present because we start processing with powders). Thus, we can have a large pressure difference that provides a large driving force. If r is ∞, then r^{-1} and ΔP are zero. The result is that we can think of the pressure above a curved surface as being different from that above a flat surface.

13.6 CAPILLARITY

We discuss wetting shortly, but you are already familiar with the capillarity effect from the traditional mercury-based or spirit-based thermometer. From Figure 13.8 we can obtain the following expression:

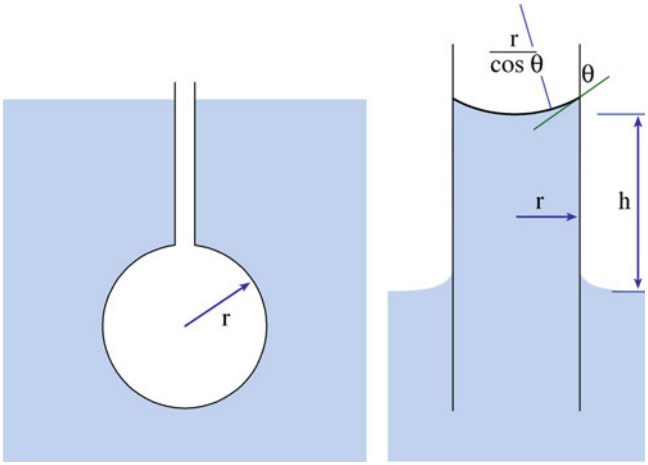

FIGURE 13.8. Geometry used to calculate the capillarity equation.

$$\Delta P = \frac{2\gamma}{r} = \gamma\frac{2\cos\theta}{r} = \rho g h \tag{13.8}$$

$$\gamma = \frac{r\rho g h}{2\cos\theta} \tag{13.9}$$

The equation $\Delta P = 2\gamma/r$ is very important because it says if $r \neq \infty$, then $\Delta P \neq$ O. The vapor pressure above a curved surface is not the same as above a flat surface due to ΔP.

$$V\Delta P = RT\ln\frac{P}{P_0} = V\gamma\left(\frac{1}{r_1}+\frac{1}{r_2}\right) \tag{13.10}$$

where V is the molar volume, P is the vapor pressure, P_0 is the vapor pressure over a flat surface, and R is the gas constant.

$$\ln\frac{P}{P_0} = \frac{V\gamma}{RT}\left(\frac{1}{r_1}+\frac{1}{r_2}\right) = \frac{M\gamma}{\rho RT}\left(\frac{1}{r_1}+\frac{1}{r_2}\right) \tag{13.11}$$

where M is the molecular weight, and ρ is the density. When $r_1 = r_2$, equation 13.15 becomes:

$$\ln\frac{P}{P_0} = \frac{V\gamma}{RT}\frac{2}{r} \tag{13.12}$$

From equation 13.12 we can see that:

- The vapor pressure of a spherical particle is a function of its radius.
- The vapor pressure at the surface of a particle is higher if r is small.

We can also show that:

- Small particles or small voids have large surface energies.
- At high temperatures, small particles tend to dissolve as the large particles grow (Ostwald ripening).
- Small particles have lower melting temperatures than large particles.

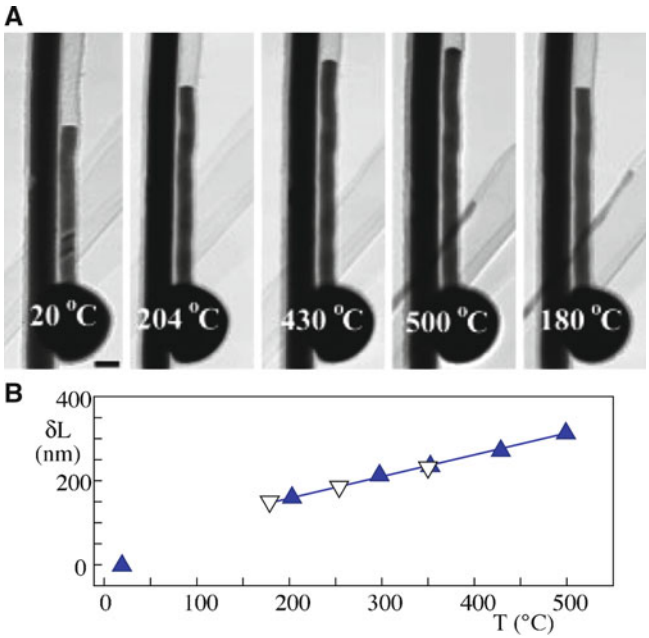

FIGURE 13.9. Capillarity effect in a silica nano-thermometer. The bar in (A) is 100 nm.

The thermometer shown in Figure 13.9 was made by filling a silica nanotube with In instead of Hg.

13.7 WETTING AND DEWETTING

The concepts of wetting and capillarity were first explained in ~1800; again, history is important in understanding the terminology. If you place drops of water on a really clean glass slide, it remains as a drop on the surface even though it develops a glass/liquid interface. If you add soap to the water, it spreads over the surface; the liquid wets the glass, and the interfacial (contact) area increases. The soap is a surfactant and lowers the energy of the glass–liquid interface. We see later that we can use surfactants to treat ceramics and liquids other than water. An example of this being used commercially for glass surfaces is the development of new auto-windshield coatings.

As usual, ceramics tend to be more complicated: at the higher temperatures encountered when processing ceramics, vaporization can also occur. At these higher temperatures the solid might not be inert, so it may react with the liquid—this is known as reactive wetting. When we talk about wetting or dewetting, it is not necessary that one of the materials is liquid (both, or neither, could be), but we do need mobility (surface diffusion) for the wetting/dewetting layer to be able to move across the surface.

The relationship between surface and interfacial energies determines, to a large extent, the wetting behavior of a liquid on a solid surface. Later we see that it also determines the phase morphology of mixtures of two or more phases. There are several interfacial tensions, γ, to contend with (they are identified by the subscripts f, s, and v, representing film, substrate, and vapor, respectively).

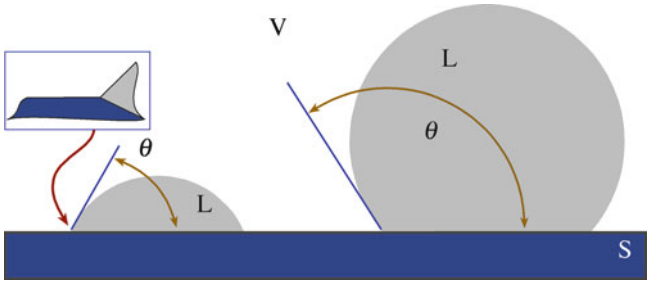

FIGURE 13.10. Drops on a solid surface, showing wetting, nonwetting, and a real equilibrium (inset).

If we consider the stable configuration of a liquid placed on a solid surface, the equilibrium shape conforms to the minimum total interfacial energy for all the phase boundaries present. If the solid–liquid interfacial energy (γ_{sl}) is high, the liquid tends to form a ball, having the minimum interfacial area, as shown in Figure 13.10 (Hg on a glass slide does this). If the liquid–vapor interfacial energy (γ_{sv}) is very small, the spreading of the liquid depends entirely on the interfacial energy (γ_{sf}), not the converse.

Young's equation relates the angle between the solid surface and the tangent to the liquid surface at the contact point. (It's a force balance in the horizontal direction because we assume the surface is not free to move in the vertical direction). This contact angle, θ, may vary between 0° and 180°. This angle specifies the conditions for minimum energy according to the relation:

$$\gamma_{ls}\cos\theta = \gamma_{sv} - \gamma_{sl} \qquad (13.13)$$

Therefore, the contact angle θ depends only on the surface properties of the involved materials. The importance of this equation is that it gives a method for comparing interfacial energies. Thomas Young first derived equation 13.13 in 1805 (Young 1805), but often it is also referred to as the Young-Dupré equation (Dupré 1869). Contact angles can be measured experimentally by the sessile drop technique. For studying the wetting of glass on a ceramic or metal surface, a small particle of the glass would be placed on the solid surface inside a tube furnace, one end of which is clear, allowing observation of the droplet (using a telemicroscope) and the contact angle as a function of temperature. Experimentally, it can be difficult to obtain reproducible values for θ. One of the problems is that of macroscopic surface roughness, which can be expressed as:

$$\cos\phi = r\cos\theta \qquad (13.14)$$

CONVENTION
The contact angle, θ, is measured "through" the liquid.

LOTUS LEAF
Water "rolls off" the leaf because the surface is rough.

where r is the roughness, ϕ is the observed contact angle, and θ is the true contact angle. The other problem is that of hysteresis: the measured angle θ depends on whether the liquid is advancing or receding.

Table 13.3 shows measured contact angles for several metals and for a basic slag (think of the slag as liquid silicate glass) on MgO single-crystal surfaces (MgO is used as a furnace lining). As noted earlier, the surface energy of solids is dependent on the crystallographic orientation, which is demonstrated by the variation in wetting angle with crystallographic planes for MgO.

Layers of glass can be deposited on polycrystalline substrates and heat-treated. The resulting faceting of the surface can be monitored while varying the annealing temperature, quench rate, etc. The glass/Al_2O_3 interfacial energy is not isotropic. An important feature of this demonstration is that the glass does affect the faceting behavior of the surface. This wetting of single surfaces by a glass is more complex than the wetting of most solids by a liquid because the glass can be very reactive at the high temperatures where the wetting actually takes place. For example, at 1,600°C a silicate glass can dissolve alumina. The situation is shown experimentally in Figure 13.11 for the (0001) and $\{10\bar{1}0\}$ surfaces: the glass/Al_2O_3 surface energy is different for different surfaces. How the glass actually dewets the surface depends on the crystal orientation of that surface.

Wetting/dewetting is also a concern for nonoxides (especially when you want to join them to other materials), and for metal/ceramic interfaces such as the metal/Si, metal/SiO_2 and metal/Si_3N_4 interfaces in the electronics industry and systems such as Al/Al_2O_3, which is important in protecting metals against corrosion.

TABLE 13.3 Measured Contact Angles of Liquids on Single-Crystal MgO

Liquid	*Test temp. (°C)*	*(100)*	*(110)*	*(111)*
Cu	1,300	106	159	149
Ag	1,300	136	141	147
Co	1,600	114	153	144
Fe	1,600	59	110	90
Basic slag[a]	1,400	9	17	32

[a]Composition: 40% SiO_2, 20% Al_2O_3, 40% CaO

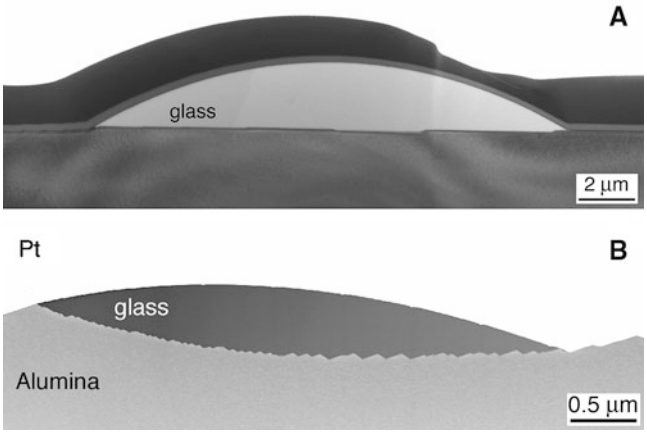

FIGURE 13.11. Experimental observations of glass droplets on the surface of Al_2O_3: (A) c-plane. (B) m-plane.

13.8 FOAMS

Foams have been known forever and studied for over a century. They are hot topics in coffee shops and cosmology but are not so well known in ceramics. When they are discussed in ceramics, they are not necessarily recognized as such, as is the case with pumice (more in Chapter 21). These cellular ceramics are also referred to as microporous or macroporous ceramics depending on the size of the cells. The common feature of these materials is that they consist of thin membranes of ceramic that enclose pores of various sizes. Thus, they have a large surface and are lightweight, but they still retain many of the properties of the ceramic. They are rigid, can be used to relatively high temperatures, and can be quite inert to chemical reactions.

Many cellular ceramics, such as the foam shown in Figure 13.12, are made using natural materials such as

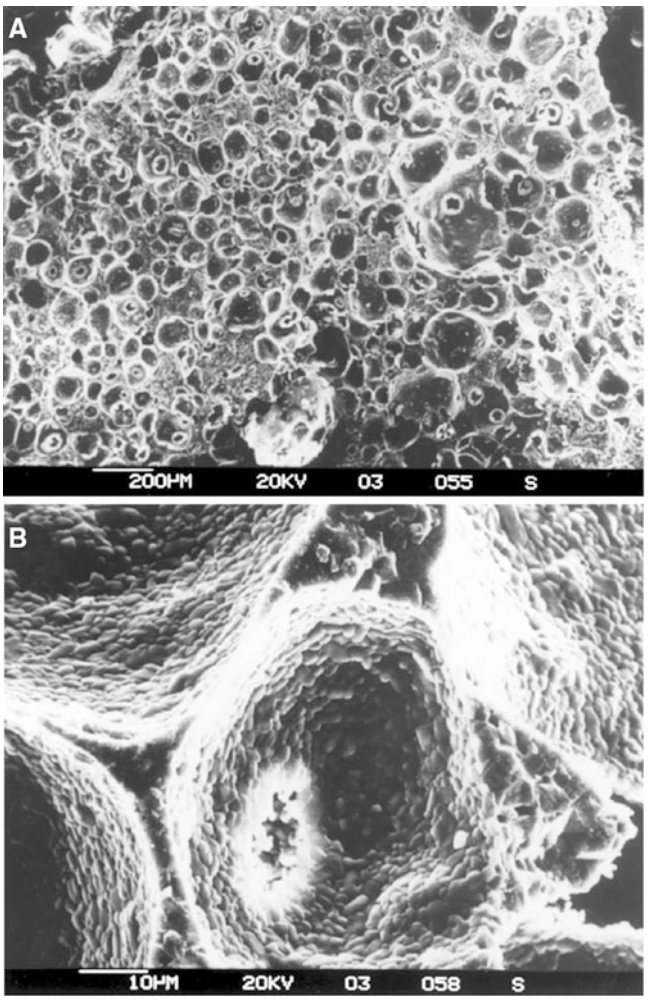

FIGURE 13.12. Surface of foam.

wood (itself a cellular material) as a template. They are biomimetic ceramics—they mimic biological materials (more in Chapter 35.) Rattan cylinders have been infiltrated with Si liquid and zeolites to make a mixed microporous/macroporous ceramic. The rattan stems were first pyrolyzed and then infiltrated with liquid Si to give the Si/SiC matrix. Finally, the internal surfaces were functionalized with a zeolite. The resulting material was tested as a catalyst for *n*-hexane cracking.

The honeycomb of the catalytic converter gives the large surface area to support the catalyst particles and ensures that the gases pass close to these particles. When used as filters, the pore (channel) diameter is engineered to suit the purpose. The synthetic bone needs the pores to encourage the intergrowth of regrowing natural bone; but if the pores are too large, then the ceramic is weakened. One technique used to provide the porous structure and the strength is to use tape casting (more in Chapter 29) to provide layers of material of different pore size, thus producing a graded porous structure.

We see these foam geometries again when we discuss glass films in grain boundaries.

13.9 EPITAXY AND FILM GROWTH

We have two immediate questions.

- What is epitaxy?
- Why discuss it here?

The reason for discussing epitaxy here is that it essentially involves depositing one material onto the surface of another. If the thin layer coating the substrate is stable, then it is wetting the substrate. If the thin layer is aligned crystallographically with respect to the substrate such that directions in the films are aligned with those in the substrate, we say the film is epitactic. In this case, it is likely to wet the substrate—the interfacial energy is relatively low. Most thin films are not epitactic.

Two ancient Greek words επι (epi—placed or resting upon) and ταξισ (taxis—arrangement) give the root of the modern word *epitaxy*, which describes an important phenomenon exhibited by thin films. Epitaxy refers to the formation of an oriented (single crystal) film on top of a crystalline substrate. Most people say epitaxial, which is grammatically incorrect but now in dictionaries. Epitaxic or epitactic would be the correct adjectives.

We discuss details (matching, chemistry, bonding, lattice matching, misfit dislocations) of such interfaces in Chapter 15 and what it means for them to be incommensurate. We also discuss there the different techniques for analyzing them. For now, we want to consider how the atomistic topography of the substrate surface influences the behavior of the film. Hence, we are concerned with surface steps and how they influence grapho-epitaxy (an alignment of the film induced by surface topography). To complicate matters further, in ceramics the film and the substrate may be amorphous, polycrystalline, or monocrystalline.

13.10 FILM GROWTH IN 2D: NUCLEATION

During film growth, atoms or molecules in the vapor phase arrive at the substrate, creating aggregates that either grow in size or disintegrate into smaller entities through dissociation processes.

Nucleate the new phase on the substrate: when an atom from the vapor strikes a solid surface, the collision decreases the energy of the atom so that it becomes partially bound to the crystal surface. Thus, any further motion of the atom is restricted to the surface of the substrate. Isolated nuclei are then formed from groups of such atoms coming together by chance through their thermal motion, as shown in Figure 13.13. Of the groups shown in Figure 13.13, a mobile "new" atom is most easily built into the crystal structure at a ledge corner as this atom interacts strongly with three neighboring atoms, and the local surface energy of the surface due to unsaturated surface bonds does not increase. Other convenient positions are sites such as Y, shown in Figure 13.13. In this way, a continuous supply of atoms leads to completion of the entire crystal plane.

Stabilize the nucleus: continuation of the growth process relies on the formation of a new stable nucleus, shown schematically as a thin cylinder. This new nucleus involves an increase in free energy due to the atoms at the edge and a decrease of free energy as the atoms are incorporated in the interior. Thus, the stability of the nucleus depends on the ratio of volume energy to surface energy. Also, there is a critical radius of the nucleus, r_c, such that if $r > r_c$ the nucleus is stable and can grow.

Grow the nuclei: if the lateral growth mechanism is relatively rapid, the rate of formation of the new nuclei on the completed planes is the decisive factor in controlling the overall growth rate.

The free energy change accompanying the formation of an aggregate of mean dimension r is given by

$$\Delta G = a_3 r^3 \Delta G_v + a_1 r_2 \gamma_{vf} + a_2 r^2 \gamma_{fs} - a_2 r^2 \gamma_{sv} \quad (13.15)$$

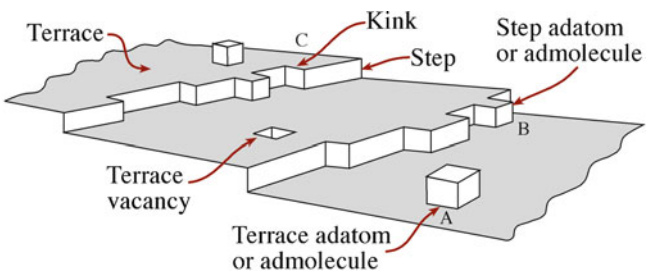

FIGURE 13.13. Surface attachment sites and the nucleation of thin films in 2D.

In Chapter 15 we consider homogeneous nucleation of a solid in a liquid. Here (using a simple qualitative model) we consider the heterogeneous nucleation of a solid film on a planar substrate.

13.11 FILM GROWTH IN 2D: MECHANISMS

The many observations of film formation have pointed to three basic growth modes that can be distinguished on the basis of equation 13.13 and are illustrated in Figure 13.14. Each mode is named after two scientists who did not necessarily work together.

- Island growth (*Volmer-Weber*). This occurs when the smallest stable clusters nucleate on the substrate surface and then grow in three dimensions to form islands. This happens when atoms or molecules in the deposit are more strongly bound to each other than to the substrate.
- Layer-by-layer growth (*Frank-van der Merwe*). Here the extension of the smallest stable nucleus occurs overwhelmingly in two dimensions, resulting in the formation of planar sheets. In this growth mode, the atoms are more strongly bound to the substrate than to each other. The first complete monolayer is then covered with a somewhat less tightly bound second layer. Provided the decrease in bonding energy is continuous toward the bulk crystal value, the layer growth mode is sustained.
- Layer-plus-island (*Stranski-Krastanow*). This growth mechanism is an intermediate combination of these two modes. In this case, after forming one or more monolayers, subsequent layer growth becomes unfavorable, and islands form. The transition from two- to three-dimensional growth is not completely understood, but any factor that disturbs the monotonic decrease in the binding energy characteristic of layer growth may be the cause.

CONTACT ANGLE AND THE MODELS

Island growth: $\theta > 0$

$$\gamma_{sv} < \gamma_{fs} + \gamma_{vf}$$

Layer-by-layer growth: $\theta = 0$. The deposit "wets" the substrate.

$$\gamma_{sv} = \gamma_{fs} + \gamma_{vf}$$

Layer-plus-island growth:

$$\gamma_{sv} > \gamma_{fs} + \gamma_{vf}$$

Growth ledges: experimentally, we know that the growth of crystals from the vapor phase often occurs at measurable rates, even at low values of supersaturation. This has been associated with growth taking place at steps provided by dislocations intersecting the interface. Such dislocations can provide a self-perpetuating source of steps as molecules are added to the crystal. The emergence point of the dislocation acquires a higher curvature until a steady state is reached in which the form of the spiral remains constant and the whole spiral rotates uniformly around the dislocation. This process was illustrated in Figure 12.25.

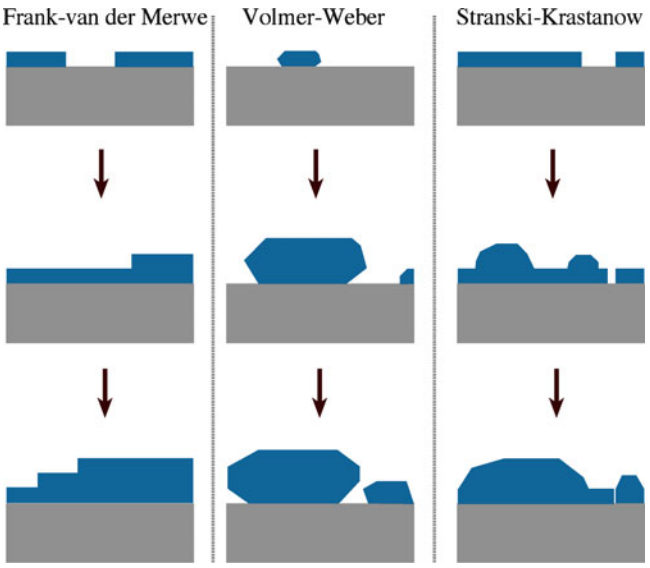

FIGURE 13.14. Three modes of thin-film growth.

ENERGY OF SITES IN FIGURE 13.13

Site	Energy Gain
A	$E_1 + 4E_2$
B	$2E_1 + 6E_2$
C	$3E_1 + 6E_2$

Experiment: start with well defined facets, so you have regions of planar surfaces. Then consider two cases.

Large entropy charge: produces smooth surfaces, faceted interfaces. Examples are growth of silicates from the melt and growth from vapor or dilute solutions.

Small entropy charge: isotropic with many growth sites. An example is the growth of a metal from the melt.

We can consider sites on the growing phase and, in a simple model (shown in Figure 13.13) of counting the nearest neighbors, assign a binding energy to each of these sites. Let E_1 be the energy of attachment at the first nearest neighbor and E_2 for the second-nearest neighbor. Then we can draw up a table for each site. You can

then determine the growth rate per unit area of interface (U), taking ν to be the usual frequency factor and a_0 the distance that the interface moves when an atom is added.

13.12 CHARACTERIZING SURFACES

The techniques for characterizing surfaces are applications or extensions of those discussed in Chapter 10. They basically fall into two groups— direct and indirect (D and I) techniques—and are summarized for surfaces in Table 13.4. Here we emphasize the application of techniques that are particularly important for ceramic surfaces. Each approach provides different information, and none answers all the questions we have. A major difficulty in studying ceramic surfaces is that many do not conduct electricity well. Thus, techniques using electron beams can have limited application. To study surfaces by transmission (TEM) or scanning (SEM) electron microscopy, we may need to coat the sample with C or even Pt to prevent charge building up on the surface and thus deflecting the electron beam. In doing so, we hope we haven't changed the surface, but of course we have.

Rather than just describe each technique, we go through a set of examples to show just what is possible with the different techniques. In each e-beam technique, coating may be necessary. The rule is: try it first, then gradually increase the thickness of the coating. In SEM, for example, lowering the kilovoltage may allow you to avoid coating altogether. Sometimes, single-crystal sapphire can be studied with TEM without coating. This possibility may depend on how clean your microscope is. You can also flash the sample with an electron beam to induce conduction for the short time that you make the observation/measurement.

Scanned probe microscopy is the method of choice for studying surfaces because to gives a direct picture of the surface and can give superb resolution, and can even give spectroscopic information. It is also much quicker, easier and cheaper than TEM.

Figure 13.15. Not only the well known semiconducting ceramics (e.g., Si, Ge, GaAs) but also the less well known but adequately conducting oxides Fe_2O_3 and NiO have been successfully imaged by scanning tunneling microscopy (STM). The main advantage of STM is that it gives better resolution normal to the plane than any other technique. Thus, we can examine the out-of-plane relaxations and rumpling that are so important in determining surface energies.

Figure 13.16. When the ceramic is not conducting, we can use atomic force microscopy (AFM) to examine the surface. The vertical resolution is not quite as good as STM, but the main loss is in the lateral resolution. This is because the geometry of the probe tip influences the image as shown in Figure 13.17. There are variations of AFM, as summarized in Section 10.6, which can give

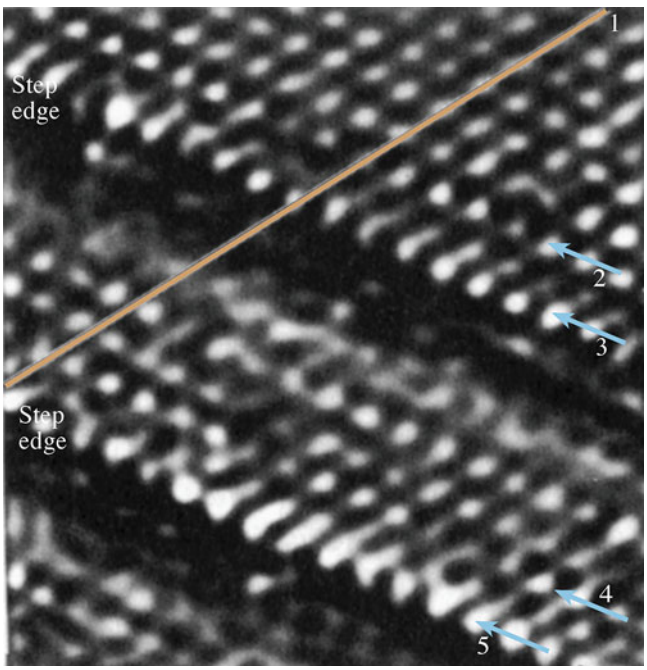

FIGURE 13.15. STM of a surface of Fe_2O_3. 1–5 indicate different rows of atoms.

TABLE 13.4 Surface Characterization Techniques

Technique		*Example*	*Special info.*	*Limitations*
AFM	D	Al_2O_3	How smooth?	V: ~0.1 nm, L: ~0.2 nm
SEM	D	Fracture	Self-selective	Structure 0.7 nm chemistry 1.5 nm
TEM	D	MgO, Al_2O_3	Faceting; plan-view	See two surfaces at same time
TEM	D	CeO_2	Faceting; profile	Must be flat, parallel to beam
TEM	D	REM	Plan-view	Tricky, foreshortens image
LEED	I	Al_2O_3	Average; vacuum	UHV technique
RHEED	I	Al_2O_3	Average; vacuum	UHV technique
STM	D	Fe_3O_4	Steps	Must conduct electrons and UHV
STM	D	Si 7 × 7	Reconstruction	UHV technique
Auger	D	La_2O_3, Y_2O_3	Chemistry	UHV technique

D direct, *I* indirect

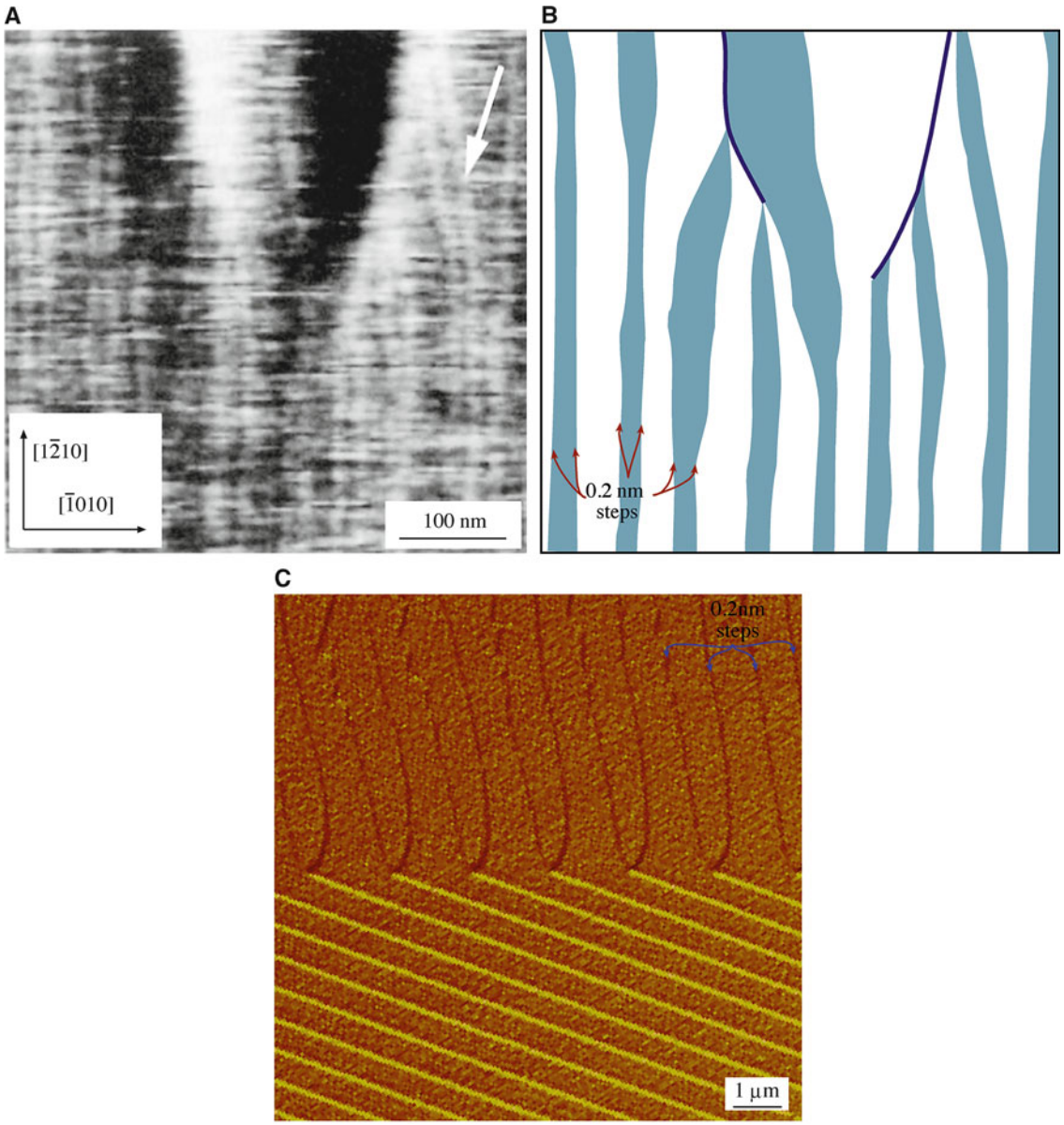

FIGURE 13.16. Sub-unit–cell surface steps. (A, B) Sapphire. (C) Spinel. The steps are 0.2 nm high in each case.

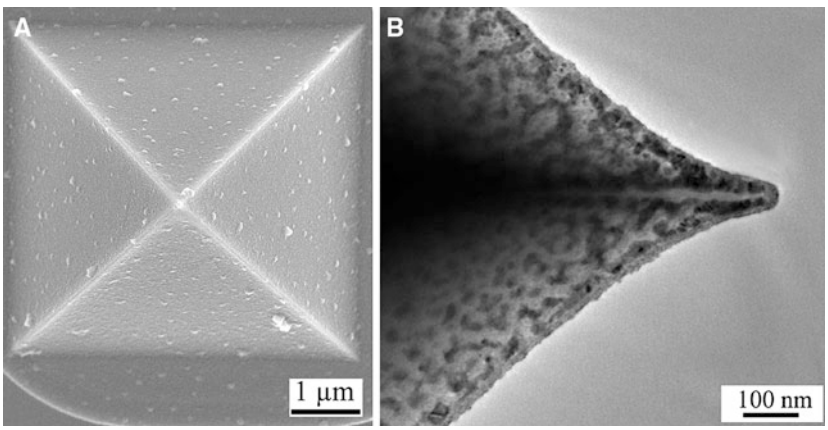

FIGURE 13.17. Electron microscopy images of atomic force microscopy (AFM) probe tips: end-on (SEM) and side view (TEM). The latter has been coated to test the interaction with the sample.

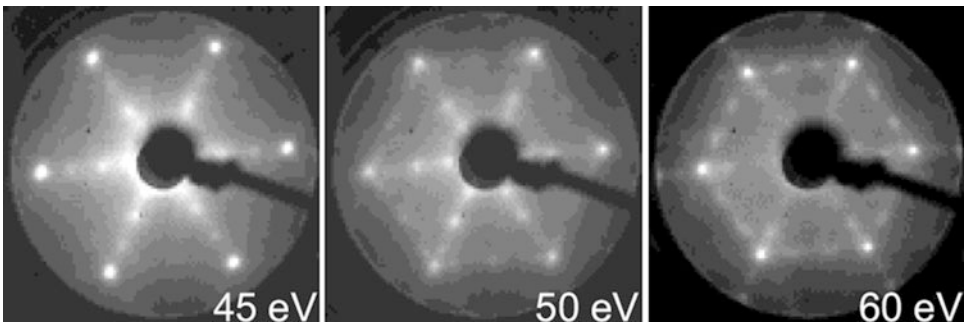

FIGURE 13.18. Low-energy electron diffraction (LEED) patterns from GaN on Al_2O_3 as the accelerating voltage is changed.

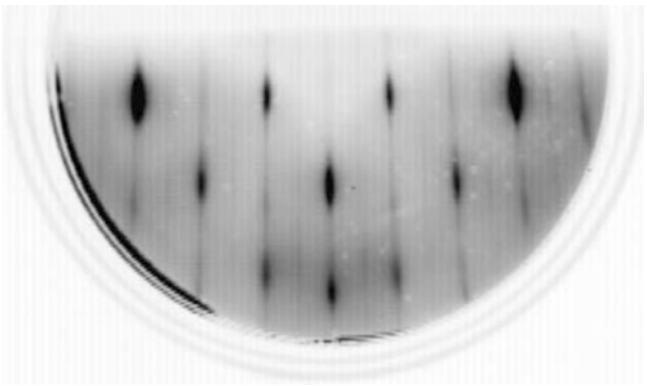

FIGURE 13.19. Reflection high-energy electron diffraction (RHEED) pattern from anatase film grown on $LaAlO_3$.

information on the magnetic fields or even the mechanical properties.

In near-field scanning optical microscopy (NSOM), we use photons to image the sample. The lateral resolution is determined by the diameter of the probe rather than by the wavelength of the light. The drawback is that the technique is rather tricky, and light may penetrate under the ceramic surface.

Diffraction techniques are the classic approach and were widely used by surface scientists before the advent of scanned probes.

Figure 13.18. Low-energy electron diffraction (LEED), as its name implies, produces data in the form of a diffraction pattern, which must then be interpreted. Because the energy of the electrons is low, the beam probes only the region closest to the surface. This is the strength of the technique, but it also means that the surface must be absolutely clean. Thus, LEED experiments are carried out in ultra-high vacuum (UHV) chambers under conditions that you never encounter in ceramics processing.

Figure 13.19. Reflection high-energy electron diffraction (RHEED) is the high-energy version of LEED. Because the electron energy is higher, the beam now probes deeper into the sample, but this is partly compensated by the beam being incident on the surface at a glancing angle. RHEED is particularly valuable during thin-film growth when the fact that it requires only a reasonably good vacuum may not be a disadvantage.

The TEM is used to study surfaces in many ways. Here we emphasize just three imaging techniques, but note that combining diffraction with imaging at near-atomic resolution in the TEM is its unique capability. We should dispel one bias immediately: TEMs can be UHV instruments. Usually, they are not operated as such because they are required to be multiuser facilities, which is usually incompatible with UHV. Therefore, even though you may see surface steps, the TEM sample usually has a layer (intentional or otherwise) of amorphous material on both surfaces. Another myth: TEM samples are so thin they do not represent the bulk. If you need a thick sample, you use a high-voltage machine where an Si TEM sample can be 5 μm thick (but you won't see atoms). Another myth: the area viewed in the TEM is tiny. Wrong—if the sample is prepared using a focused ion beam (FIB) instrument, the thin area can be >25 μm square, have a uniform thickness, and be taken from a precisely located region of a bulk sample.

Figure 13.20. Plan-view (conventional) TEM (CTEM). The electron beam is approximately normal to the plane of the thin TEM spinel and Al_2O_3 samples (although a sample may subsequently be tilted by as much as 70°).

Figure 13.21. Cross-sectional TEM (XTEM). The sample is prepared as a sandwich, and a thin section is cut to be normal to the median plane. This geometry allows us to see how features change as we move from the bulk toward the surface. It is particularly useful in thin-film growth, where we need to see the surface and how the layers developed.

Figure 13.22. Reflection electron microscopy (REM) is an old technique that was revived in the 1980s but is still not widely used. The sample is essentially bulk material with just one surface viewed. The electrons are diffracted off the surface, as in RHEED (the diffraction pattern looks just like any other RHEED pattern), and are then imaged by the TEM in the usual way. The resolution is about 0.7 nm; chemical analysis can be

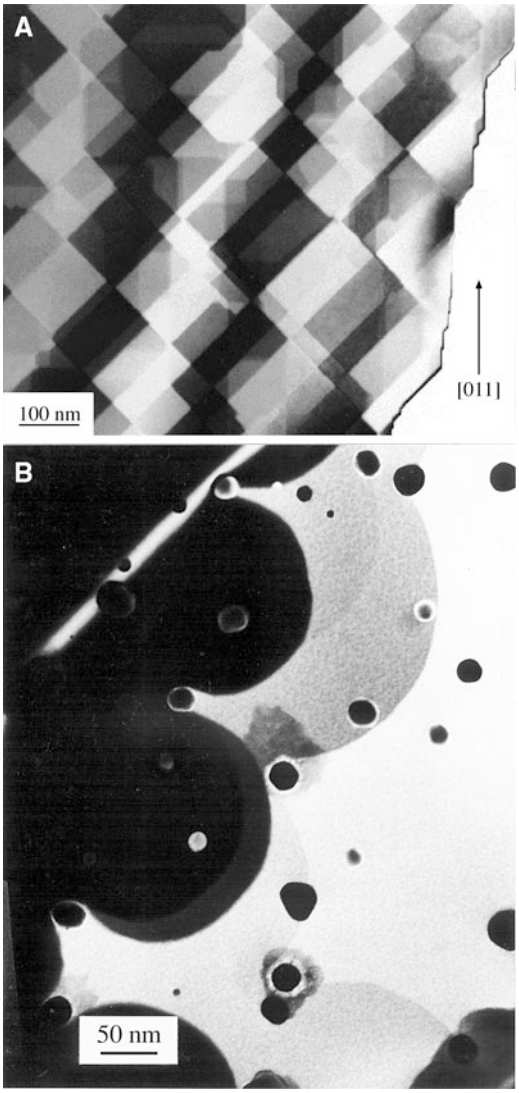

FIGURE 13.20. Plan-view TEM images of steps on $MgAl_2O_4$ and Al_2O_3. The steps occur when the thickness of the TEM sample changes abruptly.

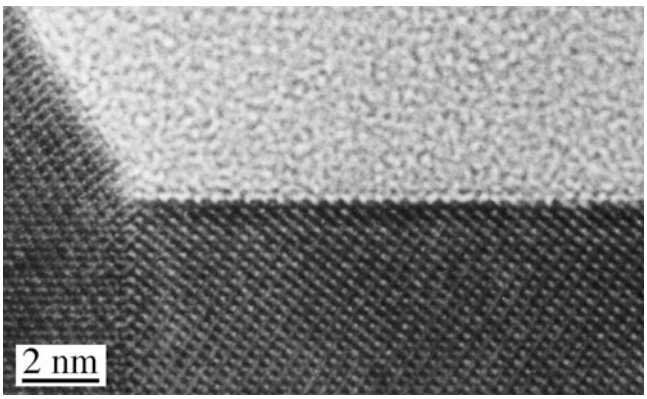

FIGURE 13.21. Cross-sectional HRTEM image of a surface of Fe_2O_3.

considered as shown by the $Al_xGa_{1-x}As/GaAs$ superlattice in this image; square millimeters of surface can be viewed just by scanning the sample. Notice the foreshortening.

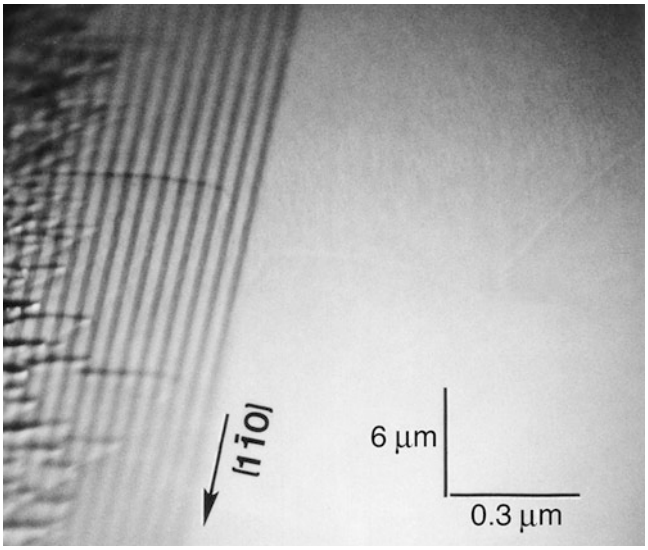

FIGURE 13.22. Reflection electron microscopy (REM) image from GaAs substrate with a $Al_xGa_{1-x}As/GaAs$ superlattice. The substrate has cleaved perfectly.

Transmission electron microscopy is a superb tool for examining surfaces of ceramics. One problem is that you always probe two surfaces at once (except with REM).

The SEM is used to study surfaces in many ways. As noted above, diffraction is also possible, and, again, SEMs can be UHV instruments. In fact, this is necessarily the case in electronics-industry semiconductor fabrication plants (FABs).

13.13 STEPS

We saw in Chapter 12 that dislocations move by the movement of jogs or kinks that are themselves defects on the dislocation. When we consider the movement of surfaces at the atomic scale, the surfaces (like dislocations) actually move by the translation of defects along them. The principle surface defects are line defects known as steps, or ledges if they are higher than a few lattice planes, and these in turn translate by kinks moving along them.

We usually assume that steps on ceramic surfaces are quite straight, as shown for spinel in Figure 13.16B, but they can appear to be smoothly curved, as seen in images of steps on the {001} surface of MgO. The lowest-energy plane for MgO is the {100} plane, which is also the cleavage plane. Some observations suggest that the {111} also has low energy, but this surface may be stabilized by water. Steps are also usually multiples of unit cells in height, but those shown in Figure 13.16A are pairs of steps on the basal plane of Al_2O_3 that are only 0.2 nm high.

Steps on MgO, wurtzite, and rutile surfaces are shown in Figure 13.23A–C. The steps on MgO show theoretically predicted displacements at the step. [Because there is a periodic set of steps, this surface could be called the (501) surface.] The special feature of the steps on the wurzite

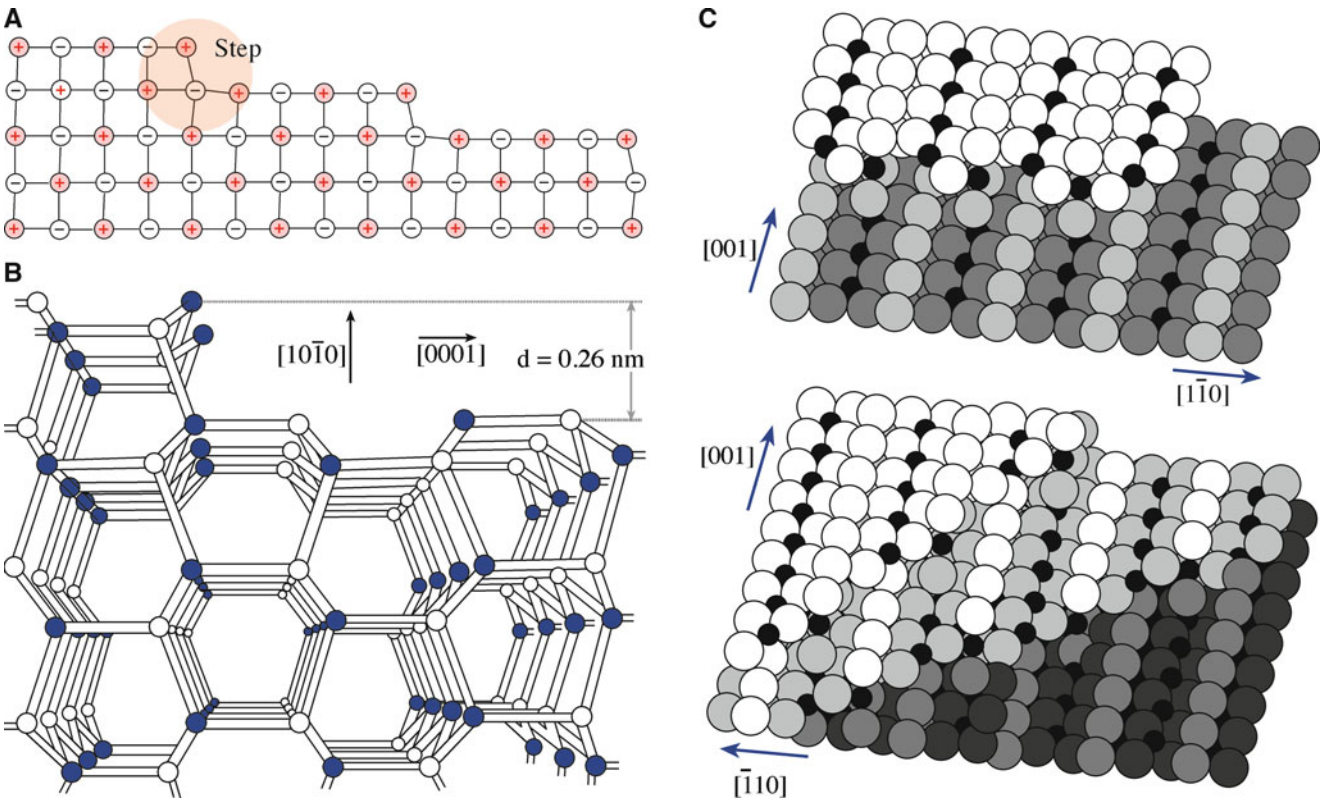

FIGURE 13.23. Representations of surface steps. (A) MgO (100) cross section. (B) Wurtzite. (C) (110) TiO_2.

surface is the presence of dangling bonds, which are localized at the step. The rutile surface shows that even when the surface is modeled using hard spheres the structure of the steps depends on their orientation. [These two vicinal surfaces could be called (223) and (443)].

13.14 IN SITU CONDITION

Many techniques can be adapted to study surfaces in situ at temperature, which is not the case for most other defects because they are not so accessible. The question is: can we learn anything new? The techniques we would most like to use are AFM and STM, neither of which is suitable because the high temperatures quickly change the probe tip. The idea of in situ observation is simply that we do not need to cool the sample to room temperature before examining it, which is a terrific advantage when materials change as we cool them. The problem is that we often cannot control the conditions (e.g., the environment) as well as we would like when making such studies because controlling the environment is often incompatible with the technique we want to use to make the observation/measurement. Electron microscopes operate best in the highest vacuum, and a glass lens placed close to an object at 1,400°C quickly degrades.

Although low-energy electron microscopy (LEEM) currently operates only at ~900°C, it could in principle go higher. LEEM is particularly attractive because it is a direct imaging technique and gives excellent resolution on the height of the steps. Use of LEEM to study the surface of TiO_2 is illustrated in Figure 13.24. Reflection electron microscopy (REM) should be able to provide similar data. The TEM can provide information on samples at temperatures up to 2,000°C, but the detail tends to become less controllable as the temperature increases. In the image shown in Figure 13.25, a film of NiO has been reduced to Ni metal while heating in the TEM at 1,000°C. New microscope holders and stages are becoming available so we will see much more use of in situ TEM in the future. Most of the work has been carried out using the SEM; environmental SEMs can heat the sample to ~1,500°C, but again the challenge is in controlling the local pO_2, etc.

13.15 SURFACES AND NANO

Surfaces are generally thought to melt before the bulk. Hence, the melting temperature of small particles is lower than that of the bulk. Such measurements can be made only while the particles are at temperature, so we know this is very difficult experimentally. In comparison, for the computer, it is quite straightforward so long as we can simulate physically meaningful situations. Computer modeling can be used to give clues, as shown in Figure 13.26, which is a case where we are not taking the environment into account. Notice that the surface gradually becomes more rounded starting at the edges.

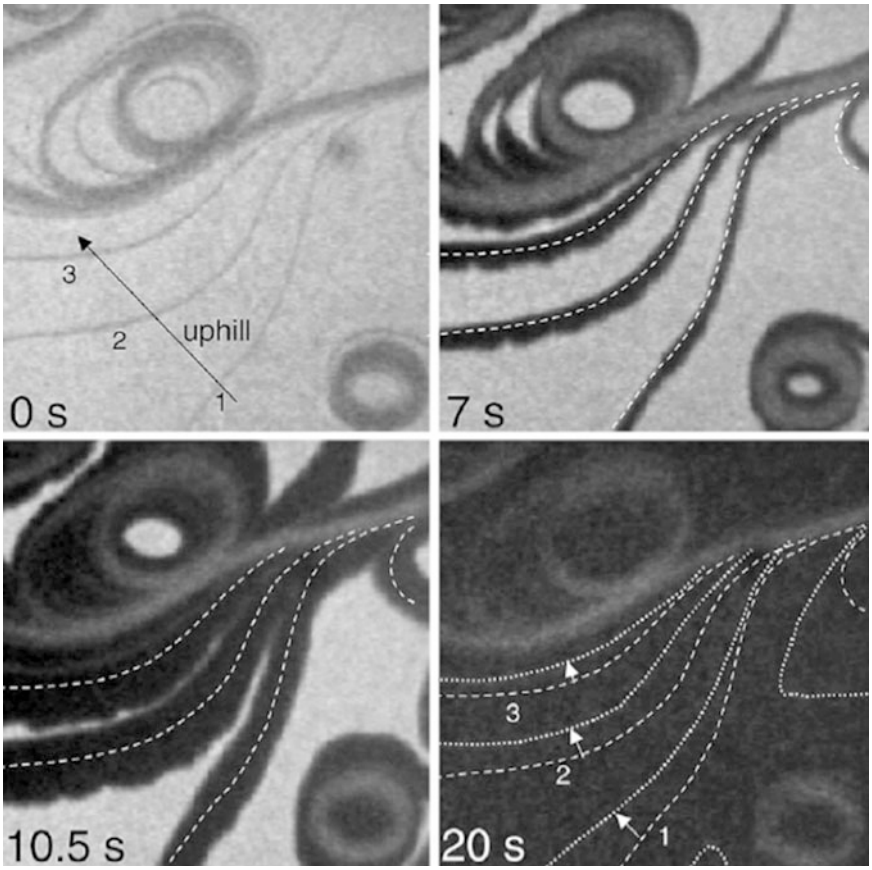

FIGURE 13.24. Studies of changes occurring at the surface of TiO_2 using low-energy electron microscopy (LEEM). A total of 20 s separates the four images. The different contrast occurs because of the surface reconstruction.

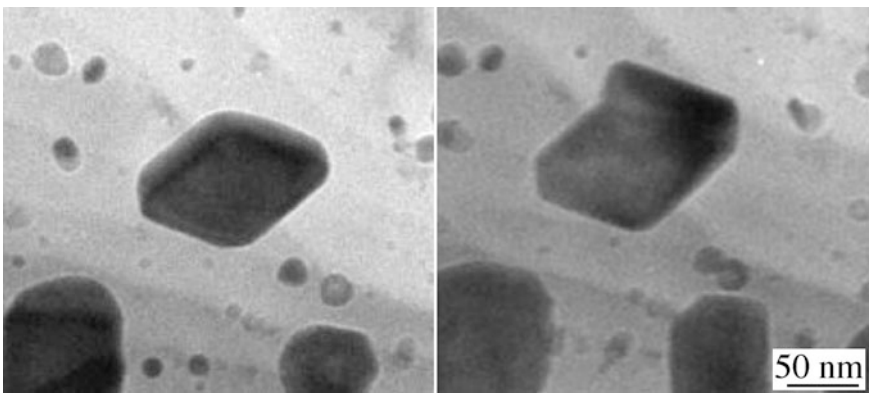

FIGURE 13.25. Changes occurring at a surface studied by in situ TEM. A NiO film had been reduced to Ni, which then dewet the sample and grew on the sapphire substrate.

The shapes shown were calculated using a potential for Au; the graphs are experimental measurements for CdS.

There are examples where the structure of a particular phase appears to be stabilized when in nanoparticle form just as some thin films can have their structure stabilized by being in contact with a substrate. Perhaps the best-known example is that γ-Al_2O_3 appears to be the stable structure at high T when in the form of nanoparticles.

13.16 COMPUTER MODELING

The use of computers to model surfaces and many other aspects of ceramics is a rapidly broadening field where great caution is always needed. Commercial software packages are now available for PCs and supercomputers. The challenge is, now, if a computer analysis is relevant to your research, how can you know if the code was right,

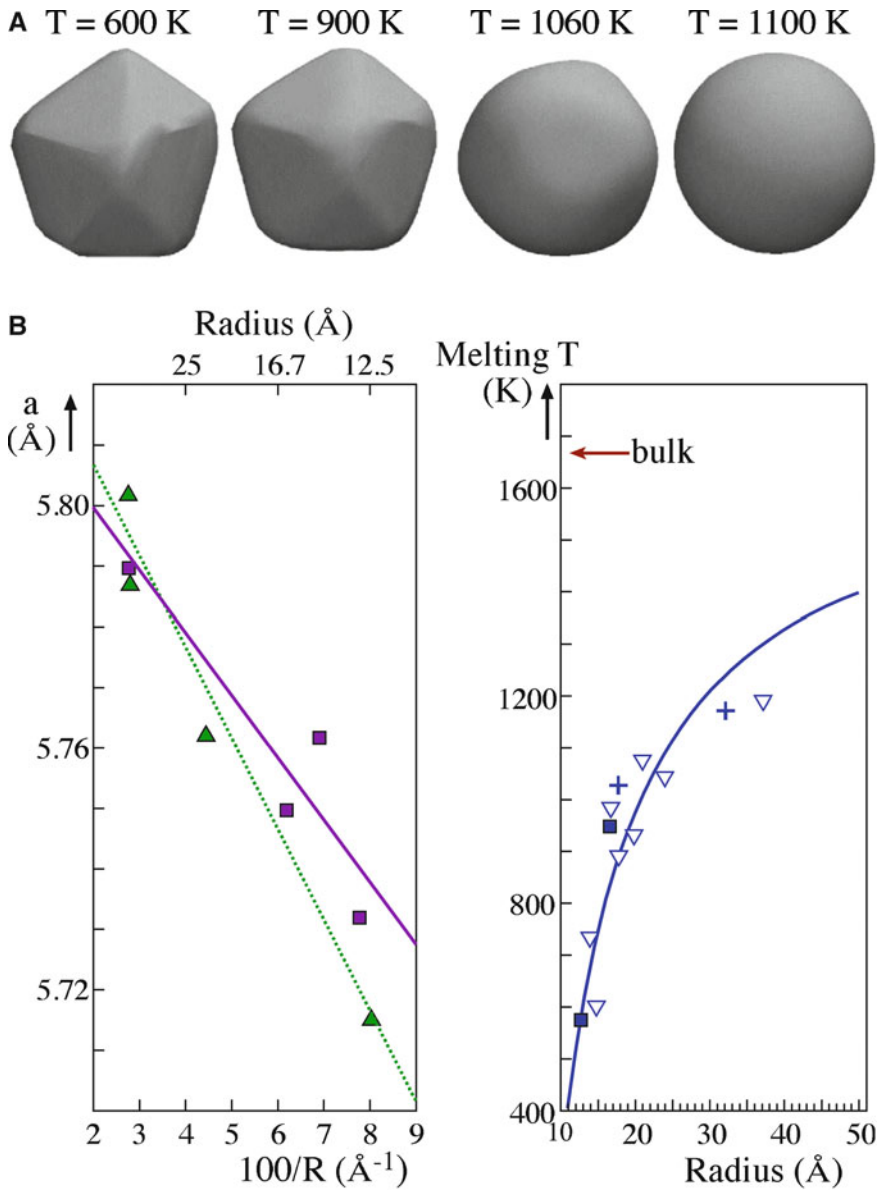

FIGURE 13.26. Nanoparticle melting. (A) Computer modeling for Au. (B) Lattice parameter and melting temperature changes as the size of CdS nanoparticles decreases.

if the program has been applied correctly, if the input data was correctly typed, what potentials were used to describe the ions, etc.? Details such as how the cell was constructed for the calculation are usually given, but it is very easy for these powerful black boxes to produce nonsensical results.

The Madelung problem for surfaces is, in one important way, more complicated than for bulk crystalline materials: a bulk sample must be neutral overall, and the positions of the ions are well defined for each unit cell, At the surface, this is not necessarily the case. MARVIN (the acronym for Minimization And Relaxation of Vacancies and Interstitials for Neutral surfaces program) is one of the best-tested software packages. The essential part of using any software package is that it must be able to reproduce some experimentally determinable facts for the material in question, which were not used as input to the program! The value of computer modeling is illustrated by a nanoparticle of SrO growing on an MgO substrate in Figure 13.27. Although the two oxides have the same structure, the SrO is slightly misoriented as it grows.

There are three distinctly different ways to terminate a (0001) surface in alumina: a single layer of Al^{3+} ions, a double layer of Al^{3+} ions, or only O^{2-} ions. This basal-plane surface of alumina has a lower energy that the rhombohedral-plane surface because the single outer layer of Al^{3+} ions can relax by moving in toward the bulk. We "know" this from computer modeling. It is very difficult to "observe" the structure experimentally.

Surface Evolver is one of structure the most fascinating freeware packages available to materials scientists. The program (by Ken Brakker) uses finite-element analysis to

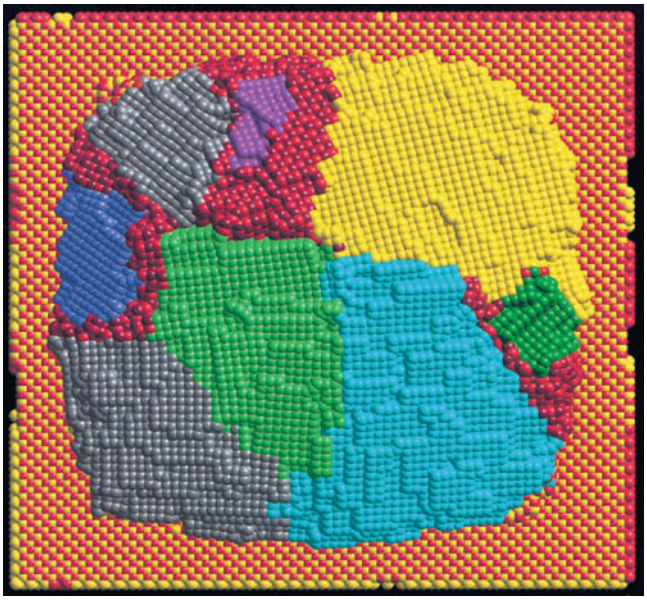

FIGURE 13.27. Computer modeling of oxide clusters on an oxide surface.

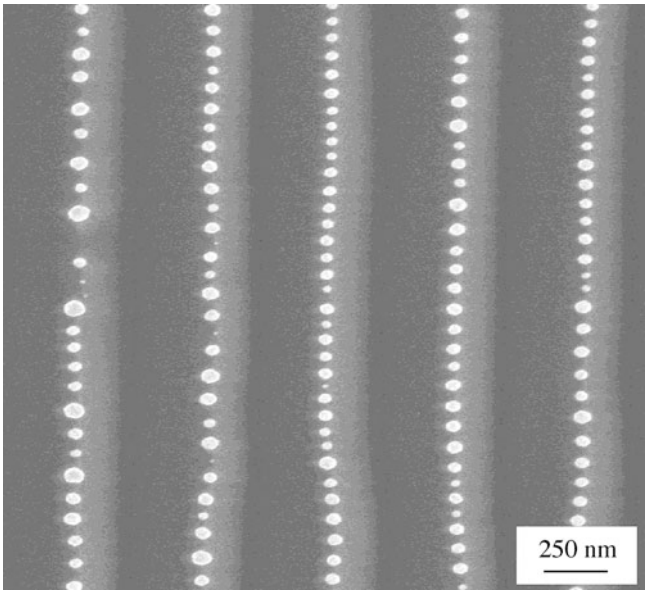

FIGURE 13.28. Self-assembly of Pt nanoparticles due to charging along a surface ridge in Al_2O_3. The particles sit on the ridge, not in the valley!

compute the morphology of surfaces that are subjected to various forces such as surface tension, interface stress, etc. It runs on most computers, not just the Mac. If you are interested in modeling droplet geometries, for example, this is the program.

Wulffman (NIST) is a software package that allows you to model the Wulff shapes of crystals interactively. You can specify the crystal symmetry. The source for NIST's Wulffman program is available for you to use (www.ctcms.nist.gov/wulffman). There are commercial programs that address the same problem.

13.17 INTRODUCTION TO PROPERTIES

The properties of ceramic surface are so broad and far reaching (as we said in the beginning) that we just give some examples, beginning with the general and becoming more specific, to emphasize this range of topics. The emphasis of this section is to introduce the fundamental ideas so that you can be aware of the possibilities and the pitfalls.

Growth. Thin films are invariably grown on surfaces.

Catalysis. A catalyst is either the surface itself, or it is supported on a surface; usually one or both of these components is a ceramic. Reactions occur at reactive sites, but the principal of catalysis is that the material facilitates, but is not chemically changed by, the process.

Joining. Materials are joined together by contacting two surfaces. In ceramics, the ionic and/or covalent nature of the bond tends to make this process more difficult than it is for metals or plastics.

Nanoparticles. The shape of a nanoparticle is determined in part by the surface energies, but the junctions between surfaces—double and triple junctions (i.e., edges and points)—become more important as the size of the particle decreases. We know very little about these surface features.

Voids. We rarely encounter real voids in ceramics except in the computer (they all contain something). They have all the challenges of particles, including the junctions, and can have nano dimensions. Generally, they have not been extensively studied experimentally because they are difficult to see!

Superconductors. The high-T_c superconductors are being used by industry but not to support high-speed trains as some had proposed in the early days. The applications often use thin films for example in superconducting quantum interference devices (SQUIDs) produced by engineering the surfaces to produce particular grain boundaries.

Surface charge. The fact that ceramic surfaces can become charged means that it is possible to align nanoparticles, for example, using this charge. That this can be achieved is illustrated in Figure 13.28 for Pt particles on Al_2O_3.

The concluding message is that we can clearly make enormous use of ceramics without understanding surfaces, but if we do understand them then we can start using ceramics to their full potential.

CHAPTER SUMMARY

The two key properties of any surface are that it has an associated energy and it is directly connected to the two media that it separates (e.g., a gas and a crystal). It is difficult to overemphasize the importance of surfaces, especially in ceramics. We can summarize some of the most important results of this chapter quite briefly.

- The energy of crystal surfaces depends on the orientation of the surface.
- There is always a tendency for a curved surface to lower its energy by becoming flat.
- The surface is critical in the growth of thin films.
- Wetting and dewetting describe the addition to or removal of material from, respectively, a surface. The important consideration is why does one, or the other, occur, and how can we make use of it.
- We can explore the surface structure and chemistry of surfaces at the atomic level because they are so accessible, but the problem is keeping them clean. In ceramic processing, surfaces are rarely clean.

In nanotechnology, surfaces become increasingly more important because a greater fraction of the atoms are at the surfaces. In the smallest nanoparticles, all the atoms may be at the surface of the particle. This property is quite closely related to a completely different group of materials, the foams. One difference between these two situations is the local curvature of the surface.

We will see in the following chapters that the surface is also critical when crystal grains join together (e.g., forming grain boundaries by sintering) or are separated (fracturing ceramics). We also mention the role of surfaces in the polishing process.

PEOPLE AND HISTORY

Binnig, Gerd. Born in Frankfurt, Germany in 1947, he joined the IBM research laboratory in Zürich in 1978. With Rohrer, he developed the scanning tunneling microscope for which they shared the 1986 Nobel Prize in Physics.

Rohrer, Heinrich. Born in St. Gallen, Switzerland in 1933. He did his PhD work at ETH (Swiss Federal Institute of Technology) on superconductivity and spent 2 years in postdoctoral studies at Rutgers University in New Jersey. In 1963 he joined the IBM research laboratory.

Young, Thomas. Born in Milverton, Somerset (UK) in 1773, he was a physicist and physician who made contributions in many areas of science. He introduced the modulus of elasticity (known also as Young's modulus) and the equation used to analyze the wetting of surfaces. His work in optics gave us Young's fringes and Young's slit. He was also an Egyptologist who helped decipher the Rosetta Stone. He died in London in 1829 and is buried in Westminster Abbey, where his epitaph states that he was "a man alike eminent in almost every department of human learning."

EXERCISES

13.1 A droplet of liquid silver is placed on an MgO substrate. The MgO(s)–Ag(l) interfacial energy is 850 mJ/m^2. (a) Calculate the contact angle of the Ag droplet. (b) Does the Ag wet the MgO? (c) If not, how might you lower the contact angle?

13.2 Repeat question 13.1 for the Al_2O_3(s)/Ag(l) system. The Al_2O_3(s)–Ag(l) system interfacial energy is 1,770 mJ/m^2.

13.3 Determine the number of free bonds/m^2 on the (100), (110), and (111) planes of germanium. The lattice parameter of Ge is 0.5658 nm.

13.4 Using equation 13.7, compare the energy of the (110) and (001) surfaces in MgO.

13.5 Can you deduce any properties about the materials from the observations and graph in Figure 13.9?

13.6 Figure 13.6B indicates that there are 74 surface atoms. How is a surface atom defined in this context?

13.7 Estimate the number of atoms in the particle imaged in Figure 13.6.

13.8 Rank the following systems in terms of increasing interface energy: Al_2O_3(s)–silicate glaze(l), Al_2O_3(s)–Pb(l), SiO_2(glass)–sodium silicate(l), and SiO_2(glass)–Cu(l). Discuss how you arrived at your ranking system, and state any assumptions that you make.

13.9 You are attempting to grow a copper thin film on MgO. What characterization technique (or techniques) might you use to determine which of the three growth modes shown in Figure 13.14 occur? What growth mechanism would you think would be most likely?

13.10 The most useful way to express surface area is in terms of m^2/g. Using these units, what is the surface area of the Pt catalyst particles in Figure 13.28?

13.11 How would you experimentally determine the contact angle?

13.12 The contact angle of iron on MgO is lower than that of the other metals given in Table 13.3. Does Fe wet MgO? Briefly explain your answer.

13.13 What would be the best technique to image a surface similar to that shown in Figure 13.13?

13.14 (a) What is the bulk melting temperature of CdS? (b) How much does the melting temperature of CdS decrease when it is in the form of 2 nm diameter nanoparticles? (c) Are there any uses for CdS nanoparticles?

13.15 A scanning electron microscope was used to examine the foam in Figure 13.12. Would a visible light (optical) microscope have produced similar images? Briefly explain your answer.

13.16 As the surface steps move in Figure 13.20B, what happens to the small dark particles on the surface?

13.17 Are the changes in the DPs in Figure 13.18 consistent with the changes in the accelerating voltage?

13.18 What is the ratio of the surface energies for the two liquids shown in Figure 13.10?

13.19 Discuss the veracity of the following statement: "MCM-41 is a ceramic foam."

13.20 Challenge: are the graph and images in Figure 13.9B what you would expect for this material. (You will want to research the original work).

GENERAL READING

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WWW

www.intelligensys.co.uk/sim/metamorph.htm (050728) is the site for MetaMorph