

Example 5-9 Silicon Device Fabrication

Devices such as transistors are made by doping semiconductors. The diffusion coefficient of phosphorus (P) in Si is $D=6.5 * 10^{-13} \text{ cm}^2 /\text{s}$ at a temperature of 1100°C . Assume the source provides a surface concentration of $10^{20} \text{ atoms}/\text{cm}^3$ and the diffusion time is one hour. Assume that the silicon wafer initially contains no P. Calculate the depth at which the concentration of P will be $10^7 \text{ atoms}/\text{cm}^3$. State any assumptions you have made while solving this problem.

SOLUTION

We assume that we can use one of the solutions to Fick's second law (i.e., Equation 5-7):

$$\frac{c_s - c_x}{c_s - c_0} = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

We will use concentrations in atoms/cm^3 , time in seconds, and D in $\frac{\text{cm}^2}{\text{s}}$ since that the left-hand side is dimensionless. Therefore, as long as we use concentrations in the same units for c_s , c_x , and c_0 , it does not matter what those units are.

$$\begin{aligned}\frac{c_s - c_x}{c_s - c_0} &= \frac{10^{20} \frac{\text{atoms}}{\text{cm}^3} - 10^{18} \frac{\text{atoms}}{\text{cm}^3}}{10^{20} \frac{\text{atoms}}{\text{cm}^3} - 0 \frac{\text{atoms}}{\text{cm}^3}} = 0.99 \\ &= \text{erf}\left[\frac{x}{2\sqrt{(6.5 \times 10^{-13} \frac{\text{cm}^2}{\text{s}})(3600 \text{ s})}}\right] \\ &= \text{erf}\left(\frac{x}{9.67 \times 10^{-5}}\right)\end{aligned}$$

From the error function values in Table 5-3 (or from your calculator computer), If $\text{erf}(z) = 0.99$, $z = 1.82$, therefore,

$$1.82 = \frac{x}{9.67 \times 10^{-5}}$$

or

$$x = 1.76 \times 10^{-4} \text{ cm}$$

or

$$x = (1.76 \times 10^{-4} \text{ cm})\left(\frac{10^4 \mu\text{m}}{\text{cm}}\right)$$

$$x = 1.76 \mu\text{m}$$

Note that we have expressed the final answer in micrometers since this is the length scale that is appropriate for this application. The main assumptions we made are (1) the D value does not change while phosphorus (P) gets incorporated in the silicon wafer and (2) the diffusion of P is only in one dimension (i.e., we ignore any lateral diffusion).

Principles of Solidification

Of all the processing techniques used in the manufacturing of materials, solidification is probably the most important? All metallic materials, as well as many ceramics, inorganic glasses, and thermoplastic polymers, are liquid or molten at some point during processing. Like water freezes to ice, molten materials solidify as they cool below their freezing temperature. In Chapter 3, we learned how materials are classified based on their atomic, ionic, or molecular order. During the solidification of materials that crystallize, the atomic arrangement changes from a short-range order (SRO) to a long-range order (LRO). The solidification of crystalline materials requires two steps. In the first step, ultra-fine crystallites, known as the nuclei of a solid phase, form from the liquid. In the second step, which can overlap with the first, the ultra-fine solid crystallites begin to grow as atoms from the liquid are attached to the nuclei until no liquid remains. Some materials, such as inorganic silicate glasses, will become solid without developing a long-range order (i.e., they remain amorphous). Many polymeric materials may develop partial crystallinity during solidification or processing. The solidification of metallic, polymeric, and ceramic materials is an important process to study because of its effect on the properties of the materials involved. In this chapter, we will study the principles of solidification as they apply to pure metals. We will discuss solidification of alloys and more complex materials in subsequent chapters. We will first discuss the technological significance of solidification and then examine the mechanisms by which solidification occurs. This will be followed by an examination of the microstructure of cast metallic materials and its effect on the material's mechanical properties.

Technological Significance

The ability to use heat to produce, melt, and cast metals such as copper, bronze, and steel is regarded as an important hallmark in the development of mankind. The use of fire for reducing naturally occurring ores into metals and alloys led to the production of useful tools and other products. Today, thousands of years later, **solidification** is still considered one of the most important manufacturing processes. Several million pounds of steel, aluminum alloys, copper, and zinc are being produced through the casting process. The solidification process is also used to manufacture specific components (e.g., aluminum alloys for automotive wheels). Industry also uses the solidification process as a **primary processing** step to produce

metallic slabs or ingots (a simple, and often large casting that later is processed into useful shapes). The ingots or slabs are then hot and cold worked through **secondary processing** steps into more useful shapes (i.e., sheets, wires, rods, plates, etc.). Solidification also is applied when joining metallic materials using techniques such as welding, brazing, and soldering. We also use solidification for processing inorganic glasses; silicate glass, for example, is processed using the float-glass process. High-quality optical fibers and other materials, such as fiberglass, also are produced from the solidification of molten glasses. During the solidification of inorganic glasses, amorphous rather than crystalline materials are produced. In the manufacture of glass-ceramics, we first shape the materials by casting amorphous glasses and then crystallize them using a heat treatment to enhance their strength. Many thermoplastic materials such as polyethylene, polyvinyl chloride (PVC), polypropylene, and the like are processed into useful shapes (i.e., fibers, tubes, bottles, toys, utensils, etc.) using a process that involves melting and solidification. Therefore, solidification is an extremely important technology used to control the properties of many melt-derived products as well as a tool for the manufacturing of modern engineered materials. In the sections that follow, we first discuss the nucleation and growth processes.

Nucleation

In the context of solidification, the term **nucleation** refers to the formation of the first nanocrystalline from molten material. For example, as water begins to freeze, nanocrystals, known as **nuclei**, form first. In a broader sense, the term nucleation refers to the initial stage of formation of one phase from another phase. When a vapor condenses into liquid, the nanoscale sized drops of liquid that appear when the condensation begins are referred to as nuclei. Later, we will also see that there are many systems in which the nuclei of a solid (β) will form from a second solid material (α) (i.e., α - to β -phase transformation). What is interesting about these transformations is that, in most engineered materials, many of them occur while the material is in the solid state (i.e., there is no melting involved). Therefore, although we discuss nucleation from a solidification perspective, it is important to note that the phenomenon of nucleation is general and is associated with phase transformations.

We expect a material to solidify when the liquid cools to just below its freezing (or melting) temperature, because the energy associated with the crystalline structure of the solid is then less than the energy of the liquid. This energy difference between the liquid and the solid is the free energy per unit volume ΔG_v and is the driving force for solidification.

When the solid forms, however, a solid-liquid interface is created (Figure 9-1(a)). A surface free energy σ_{sl} is associated with this interface. Thus, the total change in energy, shown in Figure 9-1(b), is

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \sigma_{sl}$$

where $\frac{4}{3}\pi r^3$ is the volume of a spherical solid of radius r , $4\pi r^2$ is the surface area of a spherical solid, σ_{sl} is the surface free energy of the solid-liquid interface (in this case), and ΔG_v is the free energy change per unit volume, which is negative since the phase transformation is assumed to be thermodynamically feasible. Note that σ_{sl} is not a strong function of r and is assumed constant. It has units of energy per unit area. ΔG_v also does not depend on r .

An **embryo** is a tiny particle of solid that forms from the liquid as atoms cluster together. The embryo is unstable and may either grow into a stable nucleus or redissolve.

In Figure 9-1(b), the top curve shows the parabolic variation of the total surface energy ($4\pi r^2 \cdot \sigma_{sl}$). The bottom most curve shows the total volume free energy change term ($\frac{4}{3}\pi r^3 \cdot \Delta G_v$). The curve in the middle shows the variation of ΔG . It represents the

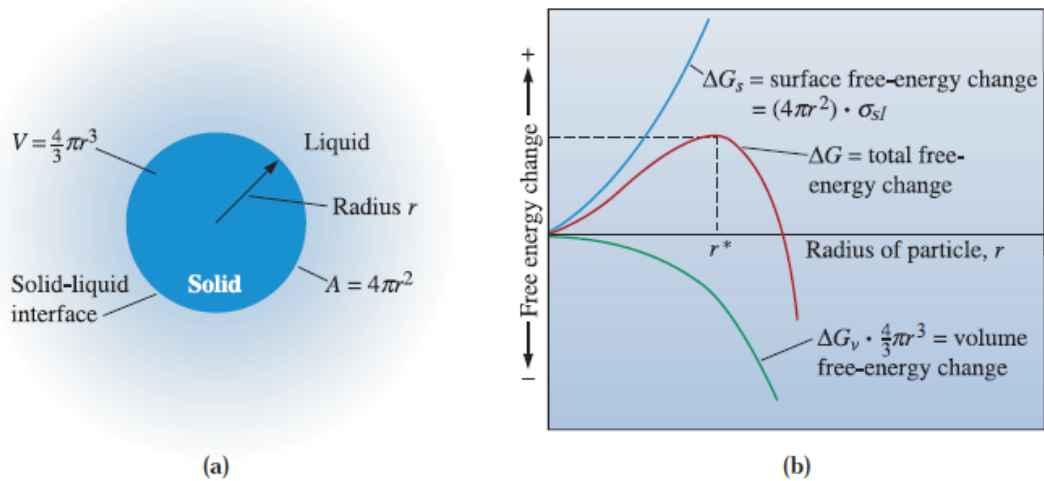


Figure 9-1 (a) An interface is created when a solid forms from the liquid. (b) The total free energy of the solid-liquid system changes with the size of the solid. The solid is an embryo if its radius is less than the critical radius and is a nucleus if its radius is greater than the critical radius.

sum of the other two curves as given by Equation 9-1. At the temperature at which the solid and liquid phases are predicted to be in thermodynamic equilibrium (i.e., at the freezing temperature), the free energy of the solid phase and that of the liquid phase are equal ($\Delta G_v = 0$), so the total free energy change (ΔG) will be positive. When the solid is very small with a radius less than the **critical radius** for nucleation (r^*) (Figure 9-1(b)), further **growth** causes the total free energy to increase. The critical radius (r^*) is the minimum size of a crystal that must be formed by atoms clustering together in the liquid before the solid particle is stable and begins to grow.

The formation of embryos is a statistical process. Many embryos form and redissolve. If by chance, an embryo forms with a radius that is larger than r^* , further growth causes the total free energy to decrease. The new solid is then stable and sustainable since nucleation has occurred, and growth of the solid particle—which is now called a nucleus—begins. At the thermodynamic melting or freezing temperatures, the probability of

forming stable, sustainable nuclei are extremely small. Therefore, solidification does not begin at the thermodynamic melting or freezing temperature. If the temperature continues to decrease below the equilibrium freezing temperature, the liquid phase that should have transformed into a solid becomes thermodynamically increasingly unstable. Because the temperature of the liquid is below the equilibrium freezing temperature, the liquid is considered undercooled. The undercooling (ΔT) is the difference between the equilibrium freezing temperature and the actual temperature of the liquid. As the extent of undercooling increases, the thermodynamic driving force for the formation of a solid phase from the liquid overtakes the resistance to create a solid-liquid interface. This phenomenon can be seen in many other phase transformations. When one solid phase (α) transforms into another solid phase (β), the system has to be cooled to a temperature that is below the thermodynamic phase transformation temperature (at which the energies of the α and β phases are equal). When a liquid is transformed into a vapor (i.e., boiling water), a bubble of vapor is created in the liquid. In order to create the transformation though, we need to **superheat** the liquid above its boiling temperature!

Therefore, we can see that liquids do not really freeze at their freezing temperature and do not really boil at their boiling point! We need to undercool the liquid for it to solidify and superheat it for it to boil!