CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-85698-0 — Modeling Materials
Continuum, Atomistic and Multiscale Techniques
Ellad B. Tadmor , Ronald E. Miller
Excerpt
More Information

1 Introduction

As we explained in the preface, modeling materials is to a large extent an exercise in multiscale modeling. To set the stage for the discussion of the various theories and methods used in the study of materials behavior, it is helpful to start with a brief tour of the structure of materials – and in particular *crystalline materials* – which are the focus of this book. In a somewhat selective way, we will discuss the phenomena that give rise to the form and properties of crystalline materials like copper, aluminum and steel, with the goal of highlighting the range of time and length scales that our modeling efforts need to address.

1.1 Multiple scales in crystalline materials

1.1.1 Orowan's pocket watch

The canonical probe of mechanical properties is the *tensile test*, whereby a standard specimen is pulled apart in uniaxial tension. The force and displacement are recorded during the test, and usually normalized by the specimen geometry to provide a plot of stress versus strain. In the discussion of an article by a different author on "the significance of tensile and other mechanical test properties of metals," Egon Orowan states: [Oro44]

> The tensile test is very easily and quickly performed, but it is not possible to do much with its results, because one does not know what they really mean. They are the outcome of a number of very complicated physical processes taking place during the extension of the specimen. The extension of a piece of metal is, in a sense, more complicated than the working of a pocket watch, and to hope to derive information about its mechanism from two or three data derived from measurements during the tensile test is perhaps as optimistic as would be an attempt to learn about the working of a pocket watch by determining its compressive strength.

It is straightforward to determine the compressive strength of a pocket watch (see Fig. 1.1). The maximum load required to crush it can be read from the graph of Fig. 1.2(a) and is 1.8 kN. But this number tells us neither anything of how a watch works under normal service conditions, nor its mechanisms of failure under compressive loads. By examining the internal structures and mechanisms, and by observing their response during the test we can start to learn, for example, how the gears interact or how the winding energy is stored. We might even be able to develop some hypotheses for how the various parts contribute to the peaks and valleys of the load versus displacement response. However, it is only

Cambridge University Press & Assessment
978-0-521-85698-0 — Modeling Materials
Continuum, Atomistic and Multiscale Techniques
Ellad B. Tadmor , Ronald E. Miller

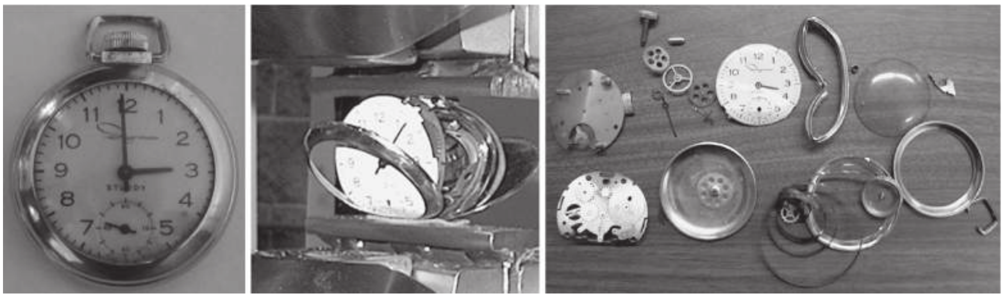
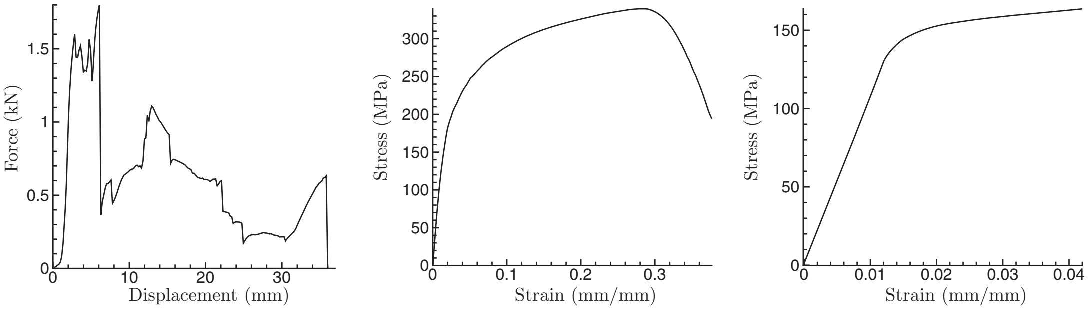


Fig. 1.1 “Orowan’s pocket watch”. An Ingraham pocket watch, circa 1960, was used to examine Orowan’s claim. A twin-column test frame (manufactured by MTS Systems Corporation), instrumented with a 100 kN load cell was used to crush the watch between two flat plates, into each of which was machined a small notch to accept the shape of the watch. The test was displacement-controlled, with a constant rate of crushing that took about 2 minutes to complete.



(a) (b) (c)

Fig. 1.2 A compressive test on a pocket watch in (a) is compared to a tensile test result for an annealed Cu–10%Ni alloy in (b) (adapted from [Cop10]) and a tensile test for compact bovine bone in (c) (adapted from [CP74, Fig. 5]).

through this combined approach of “macroscopic” testing (the curve of Fig. 1.2(a)) and “microscopic” observation and modeling (the analysis of the revealed springs and gears) that we can fully understand the pocket watch.

As Orowan suggests, the tensile test results of Figs. 1.2(b) and 1.2(c) for copper and bovine bone are not much more helpful than the pocket watch experiment in elucidating the internal microstructure[1] of these materials or how these microstructures respond to loading. Indeed, the two curves are strikingly similar aside from the differences of scale, but surely the mechanisms of failure in a metal alloy are profoundly different than those in a biological material like bone. And unlike the pocket watch, understanding the behavior of these materials requires a truly *microscopic* approach to reveal the complicated deformation mechanisms taking place in these materials as they are stretched to failure.

---

[1] The term “microstructure” refers to the internal structure of a material ranging from atomic-scale defects to larger-scale defect structures. In contrast, the “macrostructure” of the material (if such a term were used) would be the shape that the material is made to adopt as part of its engineering function.

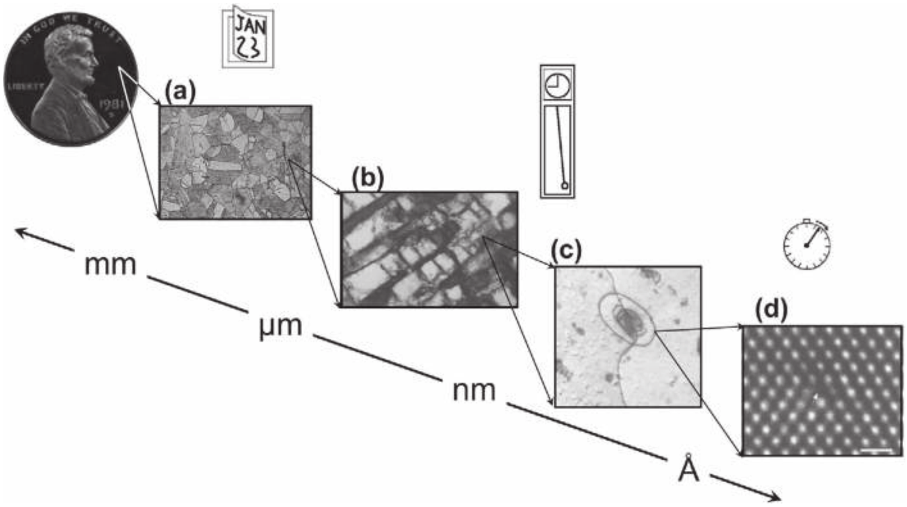


Fig. 1.3 Length and time scales in a copper penny. The macroscopically uniform copper has: (a) a grain structure on the scale of 10s to 100s of micrometers, (b) a dislocation cell structure on the scale of micrometers and (c) individual dislocations and precipitates on the nanometer scale. In (d), high-resolution transmission electron microscopy resolves individual columns of atoms in the dislocation core. This core structure has features on the ångstrom scale that affect the macroscopic plastic response. (Reprinted from: (a) [Wik08] in the public domain, (b) [GFS89] with permission of Elsevier, (c) [HH70] with permission of Royal Society Publishing and (d) [MDF94] with permission of Elsevier.)

Orowan's words sum up neatly the challenge of modeling materials. The macroscopic behavior we observe is built up of the intricate, complex interactions between mechanisms operating on a wide range of length and time scales. Studying a material from only the largest of scales is like studying a pocket watch with only a hammer; neither method will likely show us why things behave as they do. Instead, we need to approach the problem from a variety of observational and modeling perspectives and scales. Let us focus on just the question of deformation in crystalline materials, and look more closely at the operative length and time scales in the tensile stretching of a ductile metal like copper.

1.1.2 Mechanisms of plasticity

Whether we are considering the common tensile test or the complex minting of a coin, the same processes control the flow of deformation in crystalline materials like copper. The minting of the penny in Fig. 1.3 is a problem best studied with continuum mechanics, whereby the deformation can be predicted by a flow model driven by the stresses introduced by the die.[2] Such continuum modeling is the detailed subject of the companion volume

---

[2] The fact that the penny shown in Fig. 1.3 was minted in 1981 is no accident. Most pennies produced before 1982 were made of bronze (a copper alloy), and therefore the final microstructure (microscale arrangement of structures and defects in the material) is primarily that of cold-worked copper. Modern pennies, however, are actually composed of a zinc core that is forged and later plated with a thin layer of copper. As such, only 2.5% of the weight of a modern penny is copper, with a microstructure characteristic of plating, not cold-working.

Cambridge University Press & Assessment
978-0-521-85698-0 — Modeling Materials
Continuum, Atomistic and Multiscale Techniques
Ellad B. Tadmor , Ronald E. Miller
Excerpt
More Information

to this one [TME12], as well as the subject of the concise summary in Chapter 2. A key ingredient to continuum models is the *constitutive law* – the relationship that predicts the deformation response to stress. From the point of view of continuum mechanics, the constitutive law *is* the material. Such a law may be determined experimentally or guessed intuitively; one need not question the underlying reasons for a certain material response in order for a constitutive law to work. On the other hand, as we model ever more complex material response, we are unlikely to determine such laws from empirical evidence alone. Furthermore, such a *phenomenological* approach, i.e. an approach based purely on fitting to observed phenomena, cannot be used to predict new behaviors or to design new materials.

Examining the surface of the penny at higher and higher levels of magnification reveals the microstructural features that together conspire to give copper its characteristic flow properties. These are represented pictorially in Fig. 1.3 and discussed in more detail in the following sections. First, at the scale of 10s to 100s of micrometers, we see a distinctive grain structure. Each of the grains (consisting of a single copper crystal) deforms differently depending on its orientation relative to the loading and local constraints. Within each grain, we see patterns of dislocations on the scale of a micrometer, resulting from the interactions between dislocations and the grain structure (dislocations are the subject of Section 6.5.5). At still smaller scales, we can see individual dislocations and their interaction with other microstructure features. Finally, at the smallest scales of atoms, we see that each grain is actually a single crystal, with individual dislocations being simple defects in the crystal packing. A daunting range of time scales is also at play. Although the minting of a penny may only take a few seconds, deformation processes such as creep and fatigue can span years. At the other extreme, vibrations of atoms on a femtosecond scale (1 fs $=$ 0.000 000 000 000 001 s) contribute to the processes of solid-state diffusion that participate in these mechanisms of slow failure. Materials modeling is, at its core, an endeavor to develop constitutive laws through a detailed understanding of these microstructural features, and this requires the observation and modeling of the material at each of these different scales. In essence, this book is about the fundamental science behind such microstructural modeling enterprises.

1.1.3 Perfect crystals

It is likely that the copper in a penny started life by solidifying from the molten state. In going from the liquid to the solid state, copper atoms arrange themselves into the face-centered cubic (fcc) crystal structure shown in Figs. 1.4(a) and 1.4(b) (crystal structures are the subject of Chapter 3). While the lowest-energy arrangement of copper atoms is a single, perfect crystal of this type, typical solidification processes do not usually permit this to happen for large specimens. Instead, multiple crystals start to form simultaneously throughout the cooling liquid, randomly distributed and oriented, so that the final microstructure is *poly-granular*, i.e. it comprises the grains shown in Fig. 1.3(a), each of which is a single fcc crystal. Typical grains are 10–100 μm across and contain 10^{15} or more atoms. As such, they still represent an impressive extent of long-range order at the atomic scale, and the fcc crystal remains, by and large, the defining fine-scale structure of copper. This structure

CAMBRIDGE
Cambridge University Press & Assessment
978-0-521-85698-0 — Modeling Materials
Continuum, Atomistic and Multiscale Techniques
Ellad B. Tadmor , Ronald E. Miller
Excerpt
More Information

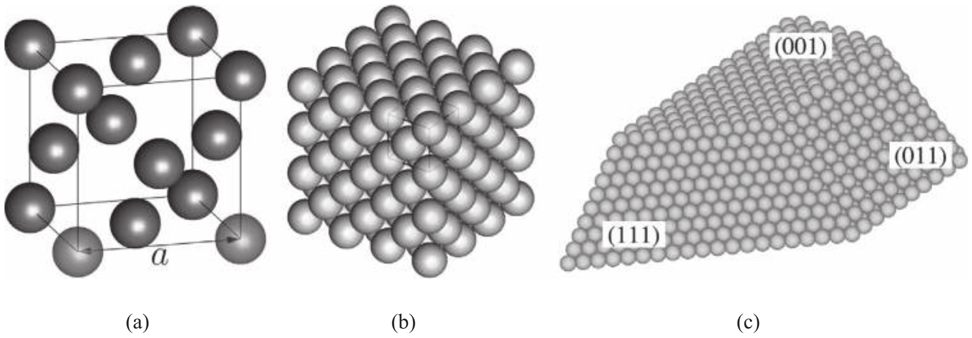
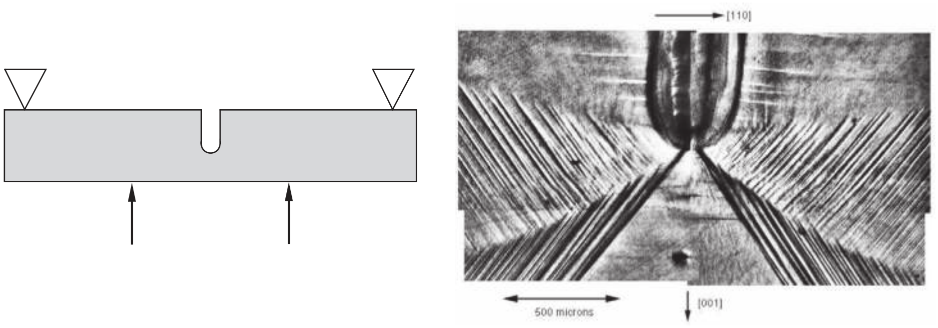


Fig. 1.4 The fcc unit cell in (a) is periodically copied through space to form a copper crystal in (b). In (c), we show three different types of free surface, indexed by the exposed atomic plane.

helps to explain the elastic properties of bulk copper, and also provides a rationale for the relatively soft, ductile nature of copper compared to other crystals. Why does copper prefer this particular crystal structure, while other elements or compounds adopt very different atomic arrangements? Why do other elements spontaneously change their crystal structure under conditions of changing temperature or stress? To understand these questions first requires modeling at the level of quantum mechanics, in order to characterize the features of bonding that make certain structures energetically favorable over others. The quantum mechanics of bonding is the subject of Chapter 4, while modeling techniques to investigate crystal structures and energetics are described in Chapter 6. Much can be gleaned about a material's properties by analyzing its overall crystal symmetry and examining the structure of its crystallographic planes. For example, the field of *crystal plasticity* is dedicated to the development of constitutive laws that predict the plastic deformation of single crystals. Some of the key physical inputs to such models are related to the so-called *slip systems*. These are the crystallographic planes and the directions on these planes along which the material can plastically deform through the passage of dislocations (a process referred to as *slip*). The number of available slip systems, their relative orientations and their respective resistances to slip deformation are determined by the structure of the underlying crystal. Thus, knowledge of the crystal structure guides us in the development of constitutive laws, dictating the appropriate symmetries and anisotropy in elastic and plastic response. Crystal structures and symmetry are the subjects of Chapter 3, while material symmetries are briefly reviewed in Section 2.5.4 (this topic is also covered in detail in the companion volume to this book [TME12]).

Figure 1.5 shows a striking manifestation of the effect of crystal structure on plastic flow. In this experiment, a large single crystal is specially prepared and notched, and the flow around the notch tip is imaged after a four-point bending test (Fig. 1.5(a)). The streaks shown in Fig. 1.5(b) are *slip lines* that form on the surface of the crystal during plastic deformation due to the motion of dislocations. As we move around the notch, we see that there are clearly different sectors that correspond to changes in the maximum stresses with respect to the orientation of the preferred slip directions in the crystal – the



(a) (b)

Fig. 1.5 (a) Schematic of a notched beam in four-point bending. (b) Slips lines formed during plastic flow around a notch (top of the picture) in a copper single crystal. The distinct sectors correspond to the activation of different slip systems as the stress changes around the notch. (Reproduced from [Shi96], with permission of Elsevier.)

orientation of these lines and the boundaries between the sectors is determined by the crystal structure.

The fcc crystal structure determines the shortest length scale of copper, which has a lattice constant of about $a = 3.6$ Å (see Fig. 1.4(a)). The lattice also determines the fastest time scales, as atomic vibrations due to thermal energy occur on a scale that is set by the bond stiffness and atomic spacing. The so-called Debye frequency, ω_{D}, provides an upper bound on the typical frequencies of atomic vibrations in a crystal, given by

$$\omega_{\mathrm{D}} = v_{\mathrm{s}} \left(\frac{3N}{4\pi V} \right)^{1/3},$$

where N/V is the number density of atoms and v_{s} is the mean speed of sound in the crystal. For copper, in which the speed of sound is about $3900\,\mathrm{m/s}$, this corresponds to a frequency on the order of 10 cycles per picosecond (ps).[3] In other words, each oscillation of an atom about its equilibrium position takes a mere 0.1 ps. This number is important because it puts limits on the types of processes we can model using molecular dynamics (MD) simulations – any discrete time integration must take timesteps that are no longer than about a tenth of this oscillation time (MD is the subject of Chapter 9). On the other hand, these rapid oscillations mean that over time scales on the order of seconds, the number of vibrations is huge. It is the largeness of these numbers – the number of atoms and the number of oscillations – that accounts for the accuracy of statistical mechanics approaches (see Chapter 7) and leads to the microscopic origins of stress which is discussed in Chapter 8.

Although the perfect fcc structure explains many properties, it is far from the only factor in determining the behavior of copper. Much of the story comes not from the perfect crystal, but from *crystal defects*, such as free surfaces, grain boundaries, dislocations and vacancies. Let us consider each of these defects in turn.

---

[3] A picosecond is 10^{-12} seconds.

Cambridge University Press & Assessment
978-0-521-85698-0 — Modeling Materials
Continuum, Atomistic and Multiscale Techniques
Ellad B. Tadmor , Ronald E. Miller
Excerpt
More Information

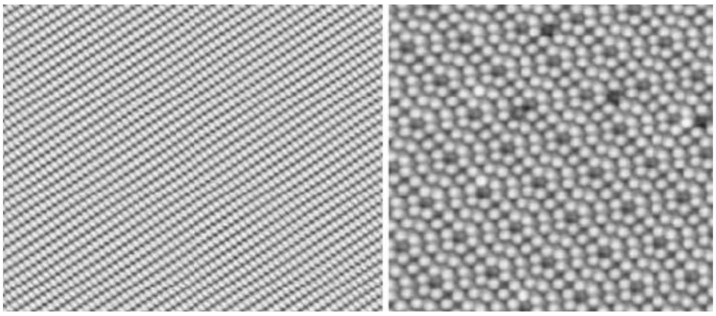

(a) (b)

Fig. 1.6 STM atomic scale images of: (a) the (110) surface of Ag and (b) the (111) surface of Si. The width of view in each image is about 15 nm. (Reprinted from [Kah10] with the kind permission Professor Antoine Kahn.)

1.1.4 Planar defects: surfaces

The fact that even a defect-free crystal is finite means that free surfaces are ever-present in crystalline solids. We can imagine cleaving the crystal of Fig. 1.4(b) along any one of an infinite number of possible planes to create different arrangements of atoms at the surface. Three examples are shown in Fig. 1.4(c). Looking carefully at this figure reveals the distinct arrangements of the atoms on each of the three planes.

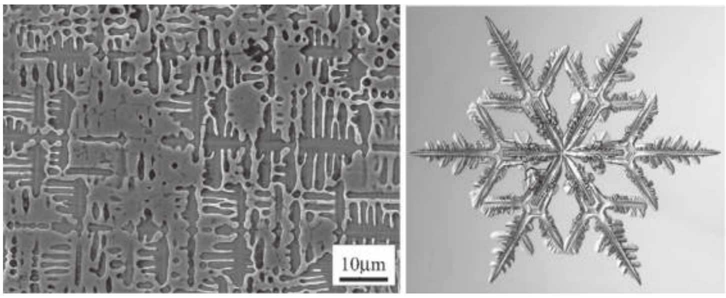
Structurally speaking, however, surfaces are more complex than merely the result of cleaving a perfect crystal. Instead, the undercoordination of surface atoms can lead to changes ranging from slight surface relaxation to dramatic reconstructions, where atoms are significantly rearranged from their bulk crystal positions. These changes in the surface structure affect such things as the reactivity of the surface with its environment, the rate at which other species of atoms may diffuse through the surface into the bulk and the mobility of atoms that are adsorbed on the surface. Materials modeling allows the direct calculation of the structure and energy of any one of these surfaces, and model calculations of surface relaxation and reconstruction have been performed for decades. More recently, experimental techniques have reached the point where the atomic surface structure can be observed directly with techniques such as scanning tunneling microscopy (STM). Some examples of STM images of surfaces (not of copper) are shown in Fig. 1.6. The images give subnanometric resolution of the surface elevation. In these examples, each hill corresponds to a single atom on an atomically flat planar surface. In Fig. 1.6(a), the (110) surface of silver shows very little difference from the ideal surface of a cleaved crystal (see Fig. 1.4(c)). On the other hand, the (111) surface of silicon shows a dramatic reconstruction that we will discuss further in Section 6.5.4. In [SK08], Salomon and Kahn used the silver surface as a template on which to grow patterns of silver nanowires.

Accurate atomic-scale calculations of the surface energy let us understand the driving forces for various materials behaviors. In Tab. 1.1, we report the surface energy values computed by Vitos *et al.* [VRSK98] for common surfaces in copper. These calculations were performed more than a decade ago using density functional theory (DFT), the subject

Cambridge University Press & Assessment
978-0-521-85698-0 — Modeling Materials
Continuum, Atomistic and Multiscale Techniques
Ellad B. Tadmor , Ronald E. Miller
Excerpt
More Information

Table 1.1. Surface energies in copper, computed using density functional theory by Vitos *et al.* [VRSK98].

	Energy/area	
Surface	$(\mathrm{J/m^2})$	$(\mathrm{meV/\AA^2})$
(111)	1.952	121.8
(011)	2.237	139.6
(001)	2.166	135.2



(a) (b)

Fig. 1.7 Dendritic growth forms: (a) $90°$ angles in cobalt and (b) $60°$ angles in ice (the snowflake shown is about 3 mm, tip-to-tip). ((a) Reproduced from [CGL$^+$07], with permission from Elsevier. (b) Reprinted from [Lib05] with permission from IOP Publishing.)

of Section 4.4. Since systems of atoms tend to want to arrange themselves into low-energy configurations, the differences in energy between surfaces favor certain morphologies over others. For instance, free surface energetics plays an important role in determining the fracture response of crystals, since fracture is, almost by definition, the creation of new surfaces. In crystals with large differences between the energy cost of different types of surface, there will be a strong anisotropy in the fracture resistance of the material. In other cases, where the energy cost to create new surfaces is high compared with other competing deformation mechanisms, a crystal may not fracture at all. Indeed, this inherent toughness is one of the desirable properties of many fcc metals.

We have already mentioned how crystals usually solidify from the molten state. Surface energetics also plays a key role in establishing the final structure of the solidified state, as grain shapes vary from being more-or-less equiaxed as in Fig. 1.3(a) to the striking dendritic examples of Fig. 1.7. Although the same material can often form either dendrites or more regular grains depending on the cooling conditions, the details of these shapes are driven by the surface energetics. For example, the normals to the orthogonally arranged (100) planes are the preferred growth directions in cubic crystals like the cobalt in Fig. 1.7(a). As a result, the dendrites form at right angles. By way of contrast, the well-known hexagonal shape of the dendrites in a snowflake (see Fig. 1.7(b)) highlights the hexagonal (instead of cubic) symmetry of the preferred growth directions in crystalline ice.

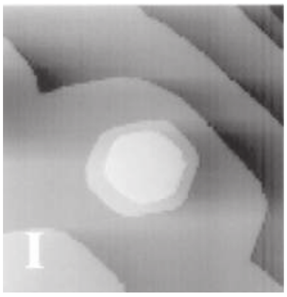


Fig. 1.8 An STM image of an island of Cu formed by vapor deposition on an atomically flat Cu (111) surface. The field of view is about 800 Å wide. (Reprinted with permission from [GIKI98], copyright 1998 by the American Physical Society.)

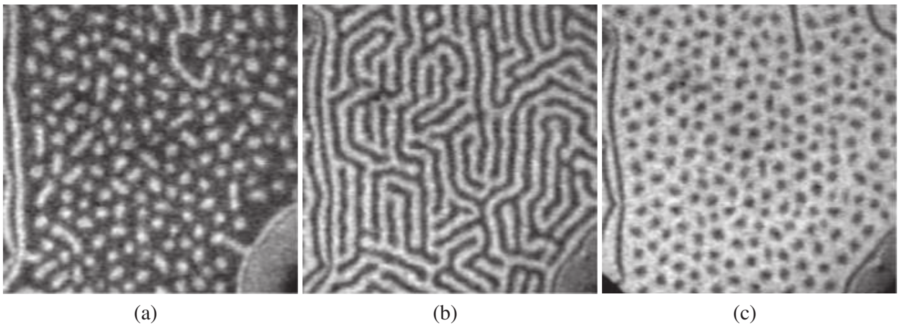
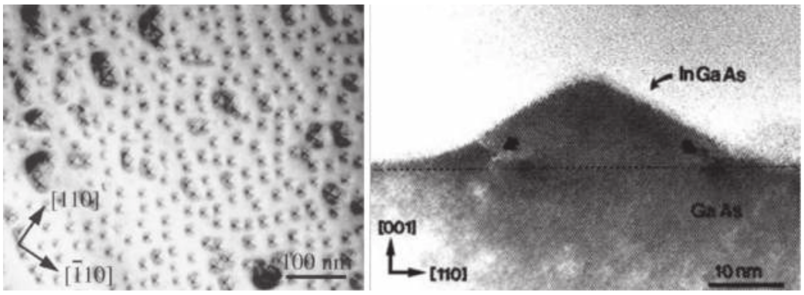

(a) (b) (c)

Fig. 1.9 Lead (light phase) deposited on copper (dark phase) can form: (a) isolated islands, (b) channels or (c) a cratered surface, depending on the amount of deposited lead. Each field of view is about 1.75 μm wide. (Reprinted from [PLBK01] with permission from Macmillan Publishers Ltd.)

As snowflakes can form directly from water vapor, so too can crystalline metals be made by depositing a vapor, atomic layer by atomic layer – a process referred to as *chemical vapor deposition*. Once again, surface energetics determines the morphology of the resulting structures and drives microstructural evolution. Figure 1.8 shows an example of the surface morphology during deposition of copper vapor onto an initially flat copper (111) surface. The steps and islands shown are each 2–4 atomic layers high, and adopt a morphology that is clearly influenced by the underlying surface structure (see the (111) face in Fig. 1.4(c)). Isolated islands like the one shown in the figure appear at a density of about 1 every 320 000 Å^2 (i.e. with an average spacing of about 600 Å). The islands then shrink or grow as atoms diffuse over the surface to lower the system energy. The rate of this process depends on the temperature and the deposition rates. For example, the white central island in Fig. 1.8 persisted for about 12 hours, slowly shrinking and changing shape due to diffusion. When this shape change led to the edge of the island contacting the edge of the larger island on which it rested, the white topmost island rapidly disappeared in less than an hour.

By depositing different atomic species, we can exploit surface energetics and morphology to cause the self-assembly of nano-scale patterns. For example, in Fig. 1.9, we show the

Cambridge University Press & Assessment
978-0-521-85698-0 — Modeling Materials
Continuum, Atomistic and Multiscale Techniques
Ellad B. Tadmor , Ronald E. Miller
Excerpt
More Information



(a) (b)

Fig. 1.10 InGaAs deposited on GaAs forms isolated islands (shown in (a) top view and (b) side view) that can be utilized as quantum dots. (Reprinted from [TF00] with permission of Elsevier.)

deposition of lead atoms on a (111) copper surface. As the amount of deposited lead increases, the pattern changes from isolated lead islands (the light phase in the images), to interconnected channels, to a regular pattern of craters in a continuous lead surface layer.[4] Scientists are trying to exploit such patterns as templates to grow nano-scale devices. In other systems, such as the growth of InGaAs on GaAs in Fig. 1.10, the resulting pattern of islands can be used as so-called quantum dots, which researchers are currently trying to exploit for the development of solid-state quantum computers. Modeling surfaces using atomistic techniques is the subject of Section 6.5.4, and there have been many studies of vapor deposition processes using MD methods (see Chapter 9).

1.1.5 Planar defects: grain boundaries

The solidification of a solid from a melt naturally leads to the formation of a microstructure consisting of single-crystal grains separated by boundaries like those in the penny in Fig. 1.3(a). At the atomic level, these *grain boundaries* are simply the junctions between two crystals – a place where the atoms must strike a structural compromise between two different orientations (see Fig. 1.11). (Grain boundary modeling is also discussed in Section 6.5.4.) Although a typical grain boundary may be only a few ångstroms across in terms of the width of the region where the atomic structure is different from the bulk, the length of a single grain boundary can extend 100s of micrometers. The distances between grain boundaries, which is of course set by the average grain size, can vary from a few nanometers to several centimeters.

Grain boundaries play a key role in many processes. For example, they act as barriers to the motion of dislocations (another type of defect discussed shortly). Because grain boundaries tend to be more open structures than the surrounding bulk crystal, they are natural sites to which impurity atoms migrate. This makes the grain boundary the formation site of second phase precipitates that can, depending on the nature of the phases, either strengthen or weaken a solid (see Fig. 1.12). Indeed, such boundary phases are so common in complex

---

[4] Between each image, approximately one lead atom to every four copper surface atoms is deposited over a time span of about 400 s. The experimental temperature was 673 K.