1 | Introduction

The history of material science is closely tied to the availablility of materials. Experiments must be done on samples. In the early days of the twentieth century, most of the available materials were found in nature. They were minerals or compounds.

1.1 1900–1910

Scanning the table of contents of the *Physical Review* for the decade 1900–1910, one finds that experiments were done on the following elements and compounds:

- Alkali metals: Na, K, Rb

- Noble metals: Cu, Ag, Au

- Divalent metals: Zn, Cd

- Multivalent metals: Al, Sn, Hg, Bi, Pb

- Transition metals: Ti, Fe, Ni, Mo, Rh, Ta, W, Ir, Pt

- Rare earth metals: Er

- Semiconductors: C, Si, Se, P

- Binary compounds: CaO, MgO, ZnS, HgS, CdS, H_2O, AgCl, AgBr, NaF, NaBr, NaCl, LiCl, KCl, TlCl, TlBr, $PbCl_2$, $PbCl_2$, PbI_2

- Oxides: KNO_3, $LiNO_3$, $NaNO_3$, $AgNO_3$, $K_2Cr_2O_2$, $NaClO_3$

The binary compounds were identified by their chemical name, such as cadmium sulfide, calcium oxide, or ice.

Table 1.1   A partial list of minerals that were used in experiments reported in the *Physical Review* during the period 1900–1910

Name	Formula
anatase	TiO_x
aragonite	$CaCO_3$
brookite	TiO_2
calcite	$CaCO_3$
cinnabar	HgS
eosin	$C_{20}H_8Br_4O_5$
fluorite	CaF_2
glass	$a\text{-}SiO_2$
pyrites	FeS_2
magnetite	Fe_3O_4
molybdenite	MoS_2
mica	silicates
quartz	SiO_2
sidot blende	ZnS

Among the most interesting materials were minerals. They were usually, and often only, identified by their mineral name. A partial list is given in table 1.1. Several minerals we were unable to identify from their names. The point of this list is that all of these compounds are found in nature as crystals. The samples were not grown in the laboratory, they were found in caves or mines. ZnS was then called sidot blende, but today is called zincblende.

A few materials were actually grown in a laboratory. One was silicon, which was grown in the research laboratory of the General Electric Company. Other artificial materials used in experiments were rubber, brass, asphalt, steel, constantan, and carborundum.

1.2 Crystal Growth

Today nearly all materials used in experiments are either grown in a laboratory or purchased from a company that grew them in a laboratory. The techniques were discovered one by one during the twentieth century. Some notable landmarks:

1. Jan Czochralski [3] invented a method of pulling crystals from their melt in 1917. His apparatus is shown in fig. 1.1. The crystals are pulled vertically, slowly, starting with a small seed crystal. Today the crystal is rotated to ensure that inhomogenieties in the liquid do not make the crystals inhomogeneous. Two-thirds of crystals are grown using the Czochralski method. Large single crystals are prepared this way. For example, silicon crystals used in the manufacturing of integrated circuits are pulled.
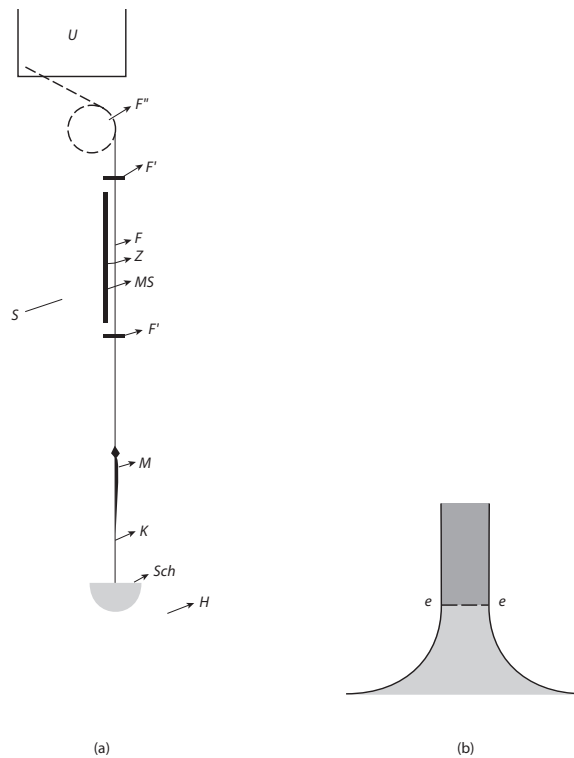
FIGURE 1.1. (a) Czochralski apparatus for pulling a crystal from the melt. Melt is at *Sch*, and a tiny seed particle (not shown) is at the end of the silk thread *K, F*. (b) Details of region where the crystal grows.

2. Percy Bridgman [2] reported the Bridgman method in 1925. A hollow cylinder is packed with powder or small crystals. It is pulled slowly through a hot region, where the material is melted and recrystalized. Large single crystals can be made this way. The cylinder can be moved vertically or horizontally.

3. William Pfann [4] invented the method of zone refining in 1952, whereby a crystal is pulled through a hot area that locally melts and recrystallizes it. Zone refining generally purifies a crystal, by pushing impurities to the end of the crystal. A crystal may be zone refined several times to obtain a low density of impurities.

4. Large single crystals may be grown from a melt. A supersturated solution of the compound will precipitate the excess material. At the right temperature, it precipitates by growing single crystals. This process happens daily in the author's pantry, as large sugar crystals are grown in the container of maple syrup. This rock candy is a family favorite.

5. Small crystals can be grown in a vapor. The material is inserted into a container, often a glass tube. Then it is heated, so the vapor is supersaturated. At the right temperature, it will grow crystals. This process is slow, but is used for laboratory samples.

The above methods are all traditional, and make three-dimensional, homogeneous samples. Many crystals today are grown using *epitaxy*. Epitaxy is the technique of growing a crystal, layer by layer, on the atomically flat surface of the same, or another, crystal. The atoms are brought to the surface by a variety of methods.

- *Molecular beam epitaxy* (MBE) uses a beam of atoms, or molecules, that are directed toward the surface. John Arthur [1] reported this method in 1968 for growing layers of GaAs. The particle beams originate in a small furnace that creates a vapor of the material, and a hole in the furnace lets atoms out. This process is very slow, but is widely practiced.

- *Chemical vapor deposition* (CVD) uses a vapor of the material in contact with the surface. This method is also called vapor-phase epitaxy (VPE).

- *Liquid phase epitaxy* (LPE) has a liquid of the material in contact with the surface. It is a variation of the solution method mentioned earlier.

1.3 Materials by Design

There are about $92 \sim 100$ stable elements in the periodic table. Around 10^4 binary compounds can be formed from pairs of different atoms. Not all pairs form a compound, but many pairs form several different crystals. Putting three elements together has about 10^6 possible compounds, and putting four elements together has about 10^8 possible compounds. The number of new materials that are grown for the first time is thousands each year. Most of these new compounds have rather ordinary properties. However, occasionally one is found that is a high-temperature superconductor, a high-field magnet, or an excellent thermoelectric. Condensed matter physics continues to be an exciting area of research, because new crystals are constantly being discovered. There seems to be no end to this process, since the number of possible new compounds is endless.

An interesting challenge is to try to make this process more efficient. At the moment the scientific community grows thousands of new materials, and a few turn out to be interesting. This process is obviously inefficient. I challenge you, the reader, to find the answer to the following questions:

- What material is the best superconductor? It would have the highest transition temperature T_c to the superconducting phase. Do not tell me the electronic properties or the best density of states. Tell me which atoms are in the crystal, and in what arrangement.

- What material is the best ferromagnet?

- What material has the best magnetoresistance? It is used in computer memories.

- What semiconductor has the highest mobility?

- What material is the best thermoelectric? Typical thermoelectrics have a high figure of merit over a limited ($\Delta T \sim 100°C$) temperature range. So there are several answers to this question for different temperature regions.

- What material is the best conductor of heat? Actually, it is probably impossible to beat diamond.

- What material has the lowest value of thermal conductivity? New low values are still being reported.

- What material is the best ferroelectric?

- What material has the best nonlinear optical properties?

All of these questions need answers. How do we invent new crystal structures that will have these desired properties?

Today the reverse process is easy. Say a new crystal is grown and its atomic coordinates are measured by x-ray scattering. Modern computer codes can

- Calculate all of the electronic energy bands.

- Calculate all of the vibrational modes (phonons).

- Calculate the transport coefficients, such as electrical resistance, Seebeck coefficient, and thermal conductivity. These coefficients determine a crystal's thermoelectric properties.

- The calculation of magnetic properties is still difficult, but is improving.

- The calculation of a crystal's superconducting properties is not yet possible.

- The calculation of its ferroelectric properties is routine by experts such as Karin Rabe or David Vanderbilt.

Given the atomic coordinates, theorists know how to calculate many of properties of the material. However, the reverse process is still not possible. We can not predict new arrangements of atoms that give a material with designed properties.

A less ambitious objective would be to predict structures of new crystals from selected elements. The prediction of crystal structure is still an art rather than a science. Given a proposed structure, the computer codes can tell whether the structure is stable, and give the dimensions of the unit cell. However, there are only a few cases where theory has dreamt up new, previously unknown, structures.

1.4 Artificial Structures

The prior section discussed designing three-dimensional, homogeneous crystals for a desired application. Another option is to design an artificially structured material.

Epitaxy can also be used to grow artificial structures such as superlattices. One band of material has n atomic layers of material A. Another band has m atomic layers of material B. Usually the material is periodic, with $n - A, m - B, n - A, m - B$, etc. The final structure has alternate bands of these two materials. If electrons, or holes, prefer to reside in band A instead of band B, they can be confined to two-dimensional motion in band A.
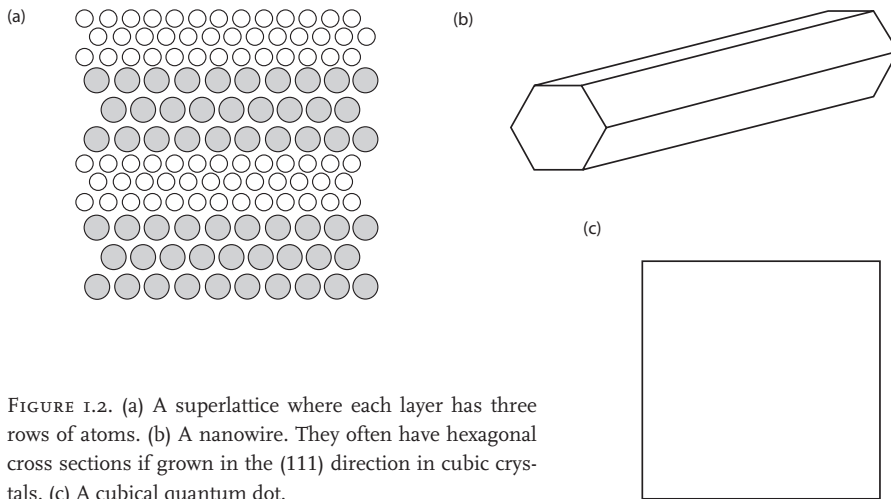
(a)

(b)

(c)

FIGURE 1.2. (a) A superlattice where each layer has three rows of atoms. (b) A nanowire. They often have hexagonal cross sections if grown in the (111) direction in cubic crystals. (c) A cubical quantum dot.

Superlattices have the property that we reduce the effective dimensionality of the motion from three to two. These interesting systems are discussed in chapter 15.

Experimentalists routinely grow nanowires of many materials using a variety of methods. The nanowires have a radius of 10–50 nm, and can have a length of many micrometers. Often they are single crystals, or contain only a few twin boundaries. In these systems the motion of the electrons, or holes, is largely one dimensional. Carbon or BN nanotubes are another type of one-dimensional conductor. These one-dimensional systems have many interesting properties, and may have useful applications in electronic devices.

Quantum dots are small nanocrystals of material. An isolated Qdot has interesting electrical properties if one can pass current through it, either by tunneling or by wire contacts. The optical properties may also be interesting. However, large crystals can be grown that are periodic arrays of Qdots: they can be two- or even three-dimensional crystals. These new systems are just starting to be investigated, and have many interesting properties. One application is to engineer photon energy gaps that trap electromagnetic radiation at selected frequencies.

Figure 1.2 shows a superlattice, a nanowire, and a Qdot. Another two-dimensional system is a single layer of carbon with the structure found in graphite. This single layer is called *graphene*. The graphene can be cut into strips, using an electron beam, and it is then a one-dimensional object. If it is cut into a finite area, it becomes a Qdot. Graphene is discussed in chapter 15.

If your goal is to design new materials with specific properties, you are not limited to three dimensions. You should consider one- and two-dimensional configurations of materials. These increase the number of options.

Nanofabrication facilities exist in many countries. They can engineer new structures. Figure 1.3 shows some typical structures produced in nanofab facilities. Figure 1.3a shows a Qdot transistor in the center. Pointed objects are gates to control electron density. Figure 1.3b shows a toadstool structure. The electrons in the circular Qdots are very isolated.
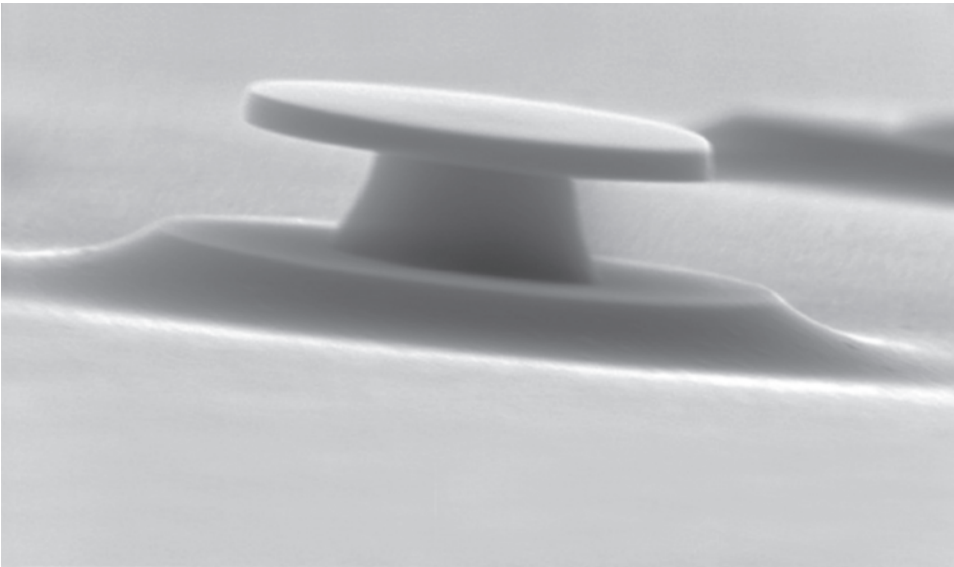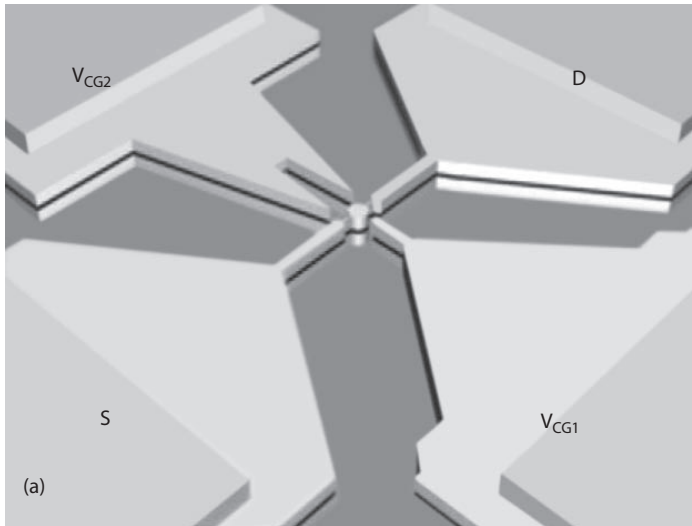
FIGURE 1.3. (a) Qdot transistor on a surface. From S. H. Son et al., *Physica E* **32**, 532 (2006). Used with permission of Elsevier. (b) Toadstool structure. Figure provided by Nitin Samarth (unpublished).

The devices shown in fig. 1.3 are only a few of many possible structures grown in nano-fab facilities. Many new types of patterns are possible, which increases the opportunity to create new types of phenomena. You, the reader, should begin to think about what new kinds of physics you can do with all of this exciting technology. Many new tools are available for the next generation of condensed matter physics.

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