

4.1 Fundamental characteristics

This chapter first identifies characteristics that distinguish smart materials from other materials, and then systematically reviews many of the more widely used ones. We begin by noting that the five fundamental characteristics that were defined as distinguishing a smart material from the more traditional materials used in architecture were transiency, selectivity, immediacy, self-actuation and directness. If we apply these characteristics to the organization of these materials then we can group them into:

- 1 Property change capability
- 2 Energy exchange capability
- 3 Discrete size/location
- 4 Reversibility

These features can potentially be exploited to either optimize a material property to better match transient input conditions or to optimize certain behaviors to maintain steady state conditions in the environment.

As we begin to explore these distinguishing characteristics, we will see that the reasons why smart materials exhibit these and other traits is not easy to explain without recourse to thinking about both the material science precepts noted in the last chapter and the specific conditions surrounding the placement and use of the material. Of particular importance is the concept of the surrounding energy or stimulus field that was discussed in Chapter 3. We recall that energy fields can be constructed of many types of energy – potential, electrical, thermal, mechanical, chemical, nuclear, kinetic – all of which can be exchanged or converted according to the First Law of Thermodynamics (the law of the conservation of energy).

The physical characteristics of smart materials are determined by these energy fields and the mechanism through which this energy input to a material is converted. If the mechanism affects the internal energy of the material by altering either the material's molecular structure or micro-structure then the input results in a *property change* of the material. If the mechanism changes the energy state of the

material composition, but does not alter the material, then the input results in an *exchange of energy* from one form to another.

A simple way of differentiating between the two mechanisms is that for property change type, the material absorbs the input energy and undergoes a change, whereas for the energy exchange type, the material stays the same but the energy undergoes a change. We consider both of these mechanisms to operate at the micro-scale, as none will affect anything larger than the molecule, and furthermore, many of the energy-exchanges take place at the atomic level. As such, we cannot 'see' this physical behavior at the scale at which it occurs.

Property change

The class of smart materials with the greatest number of potential applications to the field of architecture is the property-changing class. These materials undergo a change in a property or properties – chemical, thermal, mechanical, magnetic, optical or electrical – in response to a change in the conditions of the environment of the material. The conditions of the environment may be ambient or may be produced via a direct energy input. Included in this class are all color-changing materials, such as thermochromics, electrochromics, photochromics, etc., in which the intrinsic surface or molecular spectral absorptivity of visible electromagnetic radiation is modified through an environmental change (incident solar radiation, surface temperature) or a direct energy input to the material (current, voltage).

Energy exchange

The next class of materials that is expected to have large penetration into the field of architecture is the energy-exchanging class. These materials, which can also be called 'First Law' materials, change an input energy into another form to produce an output energy in accordance with the First Law of Thermodynamics. Although the energy conversion efficiency for smart materials such as photovoltaics and thermoelectrics is typically much less than for more conventional technologies, the potential utility of the energy is much greater. For example, the direct relationship between input energy and output energy renders many of the energy-exchanging smart materials, including piezoelectrics, pyroelectrics and photovoltaics, as excellent environmental sensors. The form of the output energy can further add direct actuation capabilities such as those currently demonstrated by electrostrictives, chemoluminescents and conducting polymers.

Reversibility/directionality

Many of the materials in the two above classes also exhibit the characteristic either of reversibility or of bi-directionality. Several of the electricity converting materials can reverse their input and output energy forms. For example, some piezoelectric materials can produce a current with an applied strain or can deform with an applied current. Materials with bi-directional property change or energy exchange behaviors can often allow further exploitation of their transient change rather than only of the input and output energies and/or properties. The energy absorption characteristics of phase-changing materials can be used either to stabilize an environment or to release energy to the environment depending on in which direction the phase change is taking place. The bi-directional nature of shape memory alloys can be exploited to produce multiple or switchable outputs, allowing the material to replace components comprised of many parts.

Size/location

Regardless of the class of smart material, one of the most fundamental characteristics that differentiate them from traditional materials is the discrete size and direct action of the material. The elimination or reduction in secondary transduction networks, additional components, and, in some cases, even packaging and power connections allows the minimization in size of the active part of the material. A component or element composed of a smart material will not only be much smaller than a similar construction using more traditional materials but will also require less infrastructural support. The resulting component can then be deployed in the most efficacious location. The smaller size coupled with the directness of the property change or energy exchange renders these materials to be particularly effective as sensors: they are less likely to interfere with the environment that they are measuring, and they are less likely to require calibration adjustments.

Type characterizations

For this discussion, we will distinguish between these two primary classes of smart materials discussed above by calling them Type 1 and Type 2 materials:

- Type 1 – a material that changes one of its properties (chemical, mechanical, optical, electrical, magnetic or thermal) in response to a change in the conditions of its

environment and does so without the need of external control.

- Type 2 – a material or device that transforms energy from one form to another to effect a desired final state.

The note in Chapter 1 on the confusion of meanings of the term 'material' is particularly relevant here. Several of the descriptions given below for these smart material types edge into what are better described as products or devices since they either consist of multiple types of individual materials or they assume a product form. For example, electrochromism is a phenomenon, but electrochromic 'materials' invariably involve multiple layers of different materials serving specific functions that enable the phenomenon to be manifest. None the less, common usage by engineers and designers would typically broadly refer to an artifact of this type as a smart 'material', largely because of the way it is used in practice.

Figure 4-1 and the following two sections briefly describe the basic characteristics of a number of common Type 1 and Type 2 smart materials. There are, of course, many others.

TYPE OF SMART MATERIAL	INPUT	OUTPUT
Type 1 Property-changing		
Thermochromics	Temperature difference	Color change
Photochromics	Radiation (Light)	Color change
Mechanochromics	Deformation	Color change
Chemochromics	Chemical concentration	Color change
Electrochromics	Electric potential difference	Color change
Liquid crystals	Electric potential difference	Color change
Suspended particle	Electric potential difference	Color change
Electrorheological	Electric potential difference	Stiffness/viscosity change
Magnetorheological	Electric potential difference	Stiffness/viscosity change
Type 2 Energy-exchanging		
Electroluminescents	Electric potential difference	Light
Photoluminescents	Radiation	Light
Chemoluminescents	Chemical concentration	Light
Thermoluminescents	Temperature difference	Light
Light-emitting diodes	Electric potential difference	Light
Photovoltaics	Radiation (Light)	Electric potential difference
Type 2 Energy-exchanging (reversible)		
Piezoelectric	Deformation	↔ Electric potential difference
Pyroelectric	Temperature difference	↔ Electric potential difference
Thermoelectric	Temperature difference	↔ Electric potential difference
Electrorestrictive	Electric potential difference	↔ Deformation
Magnetorestrictive	Magnetic field	↔ Deformation

▲ Figure 4-1 Sampling of different Type 1 and Type 2 smart materials in relation to input and output stimuli

Specific applications in design for these and other materials will be discussed in subsequent chapters.

4.2 Type 1 smart materials – property-changing

CHROMICS OR 'COLOR-CHANGING' SMART MATERIALS

Fundamental characteristics of chromics

A class of smart materials that are invariably fascinating to any designer is the so-called 'color-changing' material group which includes the following:

- *Photochromics* – materials that change color when exposed to light
- *Thermochromics* – materials that change color due to temperature changes.
- *Mechanochromics* – materials that change color due to imposed stresses and/or deformations.
- *Chemochromics* – materials that change color when exposed to specific chemical environments.
- *Electrochromics* – materials that change color when a voltage is applied. Related technologies include *liquid crystals* and *suspended particle* devices that change color or transparencies when electrically activated.

These constitute a class of materials in which a change in an external energy source produces a property change in the optical properties of a material – its absorptance, reflectance, or scattering. So-called 'color-changing' materials thus do not really change color. They change their optical properties under different external stimuli (e.g., heat, light or a chemical environment), which we often perceive as a color change. As was discussed previously, our perception of color depends on both external factors (light and the nature of the human eye) and internal factors such as those noted above. An understanding of these materials is thus more complicated than simply saying that they 'change colors'.

Recall that the external factors that affect our perception of color are many. Color is fundamentally a property of light. All incident light can be characterized by its spectral distribution of electromagnetic wavelengths. Surfaces can only reflect, absorb or transmit the available wavelengths – as such they are always subtractive. The human eye is also a subtractive surface, but does so comparatively. As a result, depending on

the spectral and intensity distributions within the field of view, color is also *relative* within the context of the human eye.

Of direct interest herein is that the observed color of an object also depends on the intrinsic optical qualities of a material. In our discussion of fundamental material properties, we noted that atomic structures include negatively charged electrons. Since light consists fundamentally of energy impulses, it reacts with the negatively charged electrons in a material. Depending on the crystalline or molecular structure of the material, the light that attempts to pass through may be delayed, redirected, absorbed or converted to some other type of energy. The precise crystalline or molecular structure of the material present will determine which of these possible behaviors will take place, and in turn determine what wavelengths of light are in some way altered (which in turn affects the perceived color of the material). Interestingly, it is the molecular structure first encountered on a material's *surface* that determines the resultant behavior. As such, thin films, coatings and paints will predominantly determine the response to light, more so than the substrate.

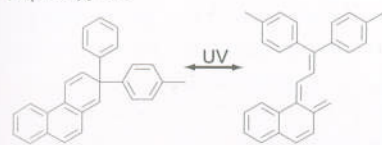
In the case of a smart material with apparent color-changing properties, the intrinsic optical properties – absorptance, reflectance, scattering – of the material are designed to change with the input of external energy. Fundamentally, the input energy produces an altered molecular structure or orientation on the surface of the material on which light is incident. The structure depends on chemical composition as well as organization of the crystal or the molecule. This external energy can be in several forms (e.g., heat or radiant energy associated with light), but in each case it induces some change in the internal surface structures of the material by reacting with the negatively charged electrons present. These changes in turn affect the material's absorptance or reflectance characteristics and hence its perceived color. These changes can be over the entire spectrum or be spectrally selective. Interestingly, these changes are reversible. When the external energy stimulus disappears, an altered structure reverts back to its original state.

The main classes of color-changing smart materials are described by the nature of the input energy that causes the property change, and include *photochromics*, *electrochromics*, *thermochromics*, *mechanochromics*, and *chemochromics*.

Photochromic materials

Photochromic materials absorb radiant energy which causes a reversible change of a single chemical species between two

Naphthopyrans

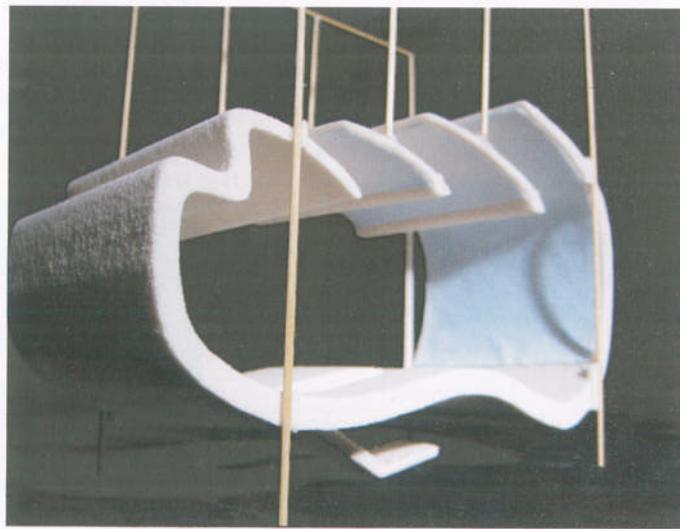


The molecular structure changes (a twisting in this case) due to exposure to the input of radiant energy from light

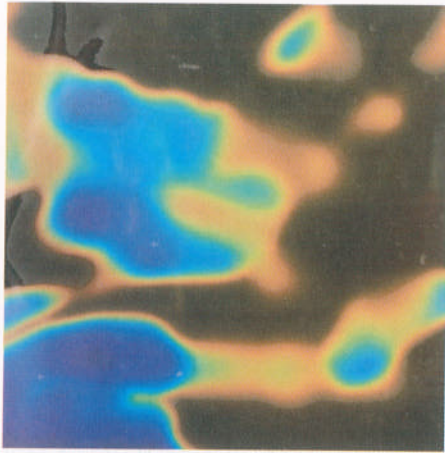
▲ **Figure 4-2** Photochromic materials change color when exposed to light (a change in the molecular structure of a photochromic material causes a change in its optical properties)

different energy states, both of which have different absorption spectra. Photochromic materials absorb electromagnetic energy in the ultraviolet region to produce an intrinsic property change. Depending on the incident energy, the material switches between the reflectively and absorptively selective parts of the visible spectrum. The molecule used for photochromic dyes appears colorless in its unactivated form. When exposed to photons of a particular wavelength, the molecular structure is altered into an excited state, and thus it begins to reflect at longer wavelengths in the visible spectrum. On removal of the ultraviolet (UV) source, the molecule will revert to its original state. A typical photochromic film, for example, can be essentially transparent and colorless until it is exposed to sunlight, when the film begins selectively to reflect or transmit certain wavelengths (such as a transparent blue). Its intensity depends upon the directness of exposure. It reverts to its original colorless state in the dark when there is no sunlight.

Photochromic materials are used in a wide range of applications. Certainly we see them used in a wide range of consumer products, such as sunglasses that change their color. In architecture, they have been used in various window or façade treatments, albeit with varying amounts of success,



▲ **Figure 4-3** Design Experiment: In the proposed 'Coolhouse', interior panels are covered with photochromic cloth that changes from a base color of white to blue upon exposure to sunlight. The panel shapes are designed for a particular solar angle for a specified time and place during the summer. At this time, the interior becomes a cool blue. In the winter, the cloth is not exposed and the interior remains white. (Teran and Teman Evans)



▲ **Figure 4-4** Thermochromic film (liquid crystal) calibrated for 25–30°C. Different colors indicate different temperature levels in the film. Blue is the highest temperature level and black is the lowest

to control solar gain and reduce glare. By and large, these applications have not proven effective because of the slowness of response and heat gain problems. Chapters 6 and 7 will treat these applications in greater detail.

Thermochromic materials

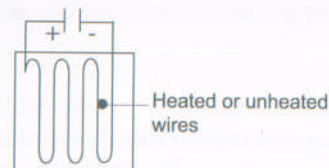
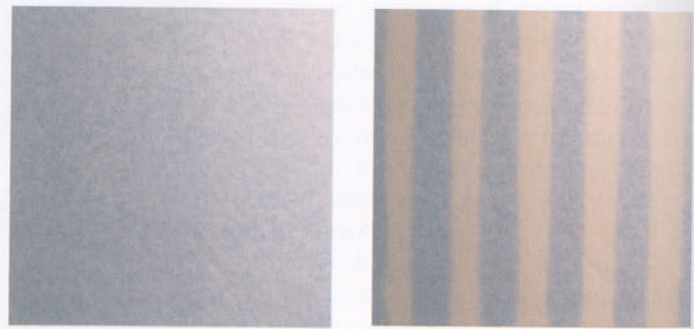
Thermochromic materials absorb heat, which leads to a thermally induced chemical reaction or phase transformation. They have properties that undergo reversible changes when the surrounding temperature is changed. The liquid crystal film versions can be formulated to change temperature from –25 to +250 °F (–30 to 120 °C) and can be sensitive enough to detect changes as small as 0.2 °F.

Thermochromic materials come in many forms, including liquid crystal forms used in thermochromic films and the leucodyes used in many other applications. Films are used in applications such as battery testers, thermometers and so forth. The widely used ‘band thermometer’ that is placed on a person’s forehead, for example, is made of thermochromic materials designed to be sensitive to particular temperature levels. A simple visual calibration device signifies the temperature level corresponding to a particular color. They can be precisely calibrated. Leucodyes, by contrast, are used in various paints and papers.

In architecture and furniture design, the seemingly never-ending quest to show the past presence of a person at a particular location or on a piece of furniture has found a new tool for expression. Several of Jurgen Mayer H.’s furniture and



▲ **Figure 4-5** Design experiment: in this simple setup, heated wires are used to generate a specific color change pattern on a thermochromic material. (Antonio Garcia Orozco)





▲ **Figure 4-6** Memories of touch via thermochromic materials. (Courtesy Juergen Mayer H)

consumer goods pieces, for example, are sensitive to body heat and show a colored 'imprint' of a person who just sat on the furniture. The image fades with time.

The notion of using thermochromic materials on the exterior of a building has similarly always aroused interest. Unfortunately, a major problem with the use of currently available thermochromic paints on the exterior is that exposure to ultraviolet wavelengths in the sun's light may cause the material to degrade and lose its color-changing capabilities.

Mechanochromic and chemochromic materials

Mechanochromics have altered optical properties when the material is subjected to stresses and deformations associated with external forces. Many polymers have been designed to exhibit these kinds of properties. The old household device for imprinting raised text onto plastic strips utilizes a plastic of this type. The raised text that results from a mechanical deformation shows through as a different color.

Chemochromics include a wide range of materials whose properties are sensitive to different chemical environments. You might perhaps recall the ancient litmus paper in a basic chemistry class.

Electrochromic materials

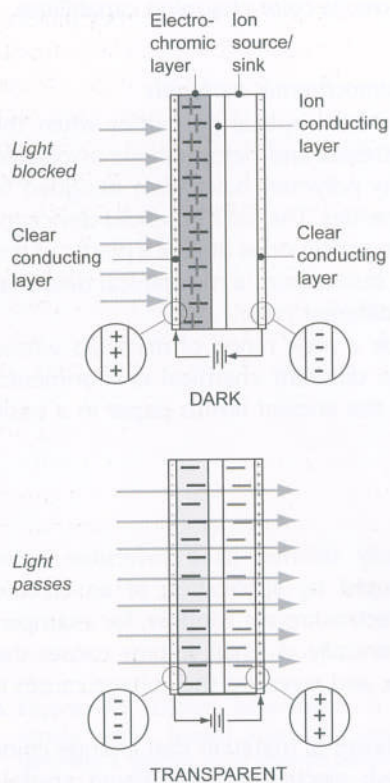
Electrochromism is broadly defined as a reversible color change of a material caused by application of an electric current or potential. An electrochromic window, for example, darkens or lightens electronically. A small voltage causes the glazing material to darken, and reversing the voltage causes it to lighten.

There are three main classes of materials that change color when electrically activated: electrochromics, liquid crystals and suspended particles. These technologies are not one-

constituent materials, but consist of multi-layer assemblies of different materials working together.

Fundamentally, color change in an electrochromic material results from a chemically induced molecular change at the surface of the material through oxidation-reduction. In order to achieve this result, layers of different materials serving different ends are used. Briefly, hydrogen or lithium ions are transported from an ion storage layer through an ion conducting layer, and injected into an electrochromic layer. In glass assemblies, the electrochromic layer is often tungsten oxide (WO_3). Applying a voltage drives the hydrogen or lithium ions from the storage layer through the conducting layer, and into the electrochromic layer, thus changing the optical properties of the electrochromic layer and causing it to absorb certain visible light wavelengths. In this case, the glass darkens. Reversing the voltage drives ions out of the electrochromic layer in the opposite direction (through the conducting layer into the storage layer), thus causing the glass to lighten. The process is relatively slow and requires a constant current.

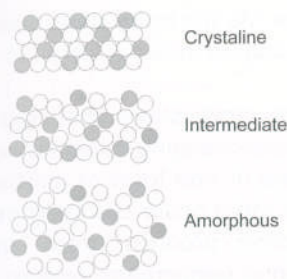
The layers forming the electrochromic component can be quite thin and readily sandwiched between traditional glazing materials. Many companies have been developing products that incorporate these features in systems from as small as a residential window to as large as the curtain wall of a building. In a typical application, the relative transparency and color tint of electrochromic windows can be electrically controlled. Note, however, that it is necessary for the voltage to remain on for the window to remain in a darkened state. This can be disadvantageous for many reasons. In Chapters 6 and 7 we will return to a discussion of the applications of electrochromic technologies.



▲ Figure 4-7 Electrochromic glass

PHASE-CHANGING MATERIALS

As discussed in the earlier section on phase changes in materials, many materials can exist in several different physical states – gas, liquid or solid – that are known as phases. A change in the temperature or pressure on a material can cause it to change from one state to another, thereby undergoing what is termed a 'phase change'. Phase change processes invariably involve the absorbing, storing or releasing of large amounts of energy in the form of latent heat. A phase change from a solid to a liquid, or liquid to a gas, and vice versa, occurs at precise temperatures. Thus, where energy is absorbed or released can be predicted based on the composition of the material. Phase-changing materials deliberately seek to take advantage of these absorption/release actions.



▲ Figure 4-8 Phase change transformation

While most materials undergo phase changes, there are several particular compositions, such as inorganic hydrated salts, that absorb and release large amounts of heat energy. As the material changes from a solid to a liquid state, and then subsequently to a gaseous state, large amounts of energy must be absorbed. When the material reverts from a gaseous to a liquid state, and then to a solid state, large amounts of energy will be released. These processes are reversible and phase-changing materials can undergo an unlimited number of cycles without degradation.

Since phase-changing materials can be designed to absorb or release energy at predictable temperatures, they have naturally been explored for use in architecture as a way of helping deal with the thermal environment in a building. One early application was the development of so-called 'phase change wallboard' which relied on different embedded materials to impart phase change capabilities. Salt hydrates, paraffins and fatty acids were commonly used. The paraffin and fatty acids were incorporated into the wallboard initially by direct immersion. Subsequently, filled plastic pellets were used. Transition temperatures were designed to be around 65–72 °F for heating dominated climates with primary heating needs and 72–79 °F for climates with primary cooling needs.

Products based on direct immersion technologies never worked well and proved to have problems of their own that were associated with the more or less exposed paraffin and fatty acids (including problems with animals eating the wallboard products). Technologies based on sealing phase-changing materials into small pellets worked better. Pellet technologies have achieved widespread use, for example, in connection with radiant floor heating systems. In many climates, radiant floor systems installed in concrete slabs can provide quite comfortable heating, but are subjected to undesired cycling and temperature swings because of the need to keep the temperature of the slab at the desired level, which typically requires a high initial temperature. Embedding phase-changing materials in the form of encased pellets can help level out these undesirable temperature swings.

Phase-changing materials have also successfully found their way into outdoor clothing. Patented technologies exist for embedding microencapsulated phase-changing materials in a textile. These encapsulations are microscopic in size. The phase-changing materials within these capsules are designed to be in a half-solid, half-liquid state near normal skin temperature. As a person exercises and generates heat, the materials undergo a phase change and absorb excess heat,

thus keeping the body cooler. As the body cools down, and heat is needed, the phase-changing materials begin to release heat to warm the body.

Of particular interest in the applications discussed is that successful applications of phase-changing materials occurred when they were encapsulated in one form or another. It is easy to imagine how encapsulated phase-changing materials could be used in many other products, from lamps to furniture, as a way of mitigating temperature swings.

CONDUCTING POLYMERS AND OTHER SMART CONDUCTORS

In this day and age of electronic devices, it is no wonder that a lot of attention has been paid to materials that conduct electricity. Any reader of scientific news has heard about the strong interest in materials such as superconductors that offer little or no resistance to the flow of electricity. In this section, however, we will look at a broader range of conducting materials, including those that offer great potential in different design applications.

In general, there is a broad spectrum associated with electrical conductivity through terms like 'insulators', 'conductors', 'semi-conductors' and 'super-conductors' – with insulators being the least conductive of all materials. Many of the products that architectural and industrial designers are most familiar with are simple conductors. Obviously, many metals are inherently electrically conductive due to their atomic bonding structures with their loosely bound electrons allowing easy electron flow through the material. As discussed in more detail in Chapter 6, many traditional products that are not intrinsically conductive, e.g., glasses or many polymers, can be made so by various means. Polymers can be made conductive by the direct addition of conductive materials (e.g., graphite, metal oxide particles) into the material. Glasses, normally highly insulating, can be made conductive and still be transparent via thin film metal deposition processes on their surfaces.

There are other polymers whose electrical conductivity is intrinsic. Electroactive polymers change their electrical conductivity in response to a change in the strength of an electrical field applied to the material. A molecular rearrangement occurs, which aligns molecules in a particular way and frees electrons to serve as electricity conductors. Examples include polyaniline and polypyrrole. These are normally conjugated polymers based on organic compounds that have internal structures in which electrons can move more

freely. Some polymers exhibit semiconductor behavior and can be light-emitting (see *Semiconductors* below and *Light-emitting polymers* in Chapter 6). Electrochemical polymers exhibit a change in response to the strength of the chemical environment present.

A number of applications have been proposed for conducting polymers. Artificial muscles have been developed using polypyrrole and polyaniline films. These films are laminated around an ion-conducting film to form a sandwich construction. When subjected to a current, a transfer of ions occurs. The current flow tends to reduce one side and oxidize the other. One side expands and the other contracts. Since the films are separated, bending occurs. This bending can then be utilized to create mechanical forces and actions.

Despite the dream of many designers to cover a building with conducting polymers, and to have computer-generated images appearing anywhere one desires, it is necessary to remember that these materials are essentially conductors only. In the same way it would not be easy to make an image appear on a sheet of copper, it is similarly difficult to make an image appear on a conducting polymer. Since films can be manipulated (cut, patterned, laminated, etc.), possibilities in this realm do exist, but remain elusive.

Other smart conductors include *photoconductors* and *photoresistors* that exhibit changes in their electrical conductivity when exposed to a light source. *Pyroconductors* are materials whose conductivities are temperature-dependent, and can have minimal conductivity near certain critical low temperatures. *Magnetoconductors* have conductivities responsive to the strength of an applied magnetic field. Many of these specialized conducting materials find applications as sensors of one type or another. Many small devices, including motion sensors, already employ various kinds of photoconductors or photoresistors (see Chapter 7). Others, including pyroconductors, are used for thermal sensing.

RHEOLOGICAL PROPERTY-CHANGING MATERIALS

The term 'rheological' generally refers to the properties of flowing matter, notably fluids and viscous materials. While not among the more obvious materials that the typical designer would seek to use, there are many interesting properties, in particular viscosity, that might well be worth exploring.

Many of these materials are termed 'field-dependent'. Specifically, they change their properties in response to electric or magnetic fields. Most of these fluids are so-called 'structured fluids' with colloidal dispersions that change

phase when subjected to an electric or magnetic field. Accompanying the phase change is a change in the properties of the fluid.

Electrorheological (ER) fluids are particularly interesting. When an external electric field is applied to an electrorheological fluid, the viscosity of the fluid increases remarkably. When the electric field is removed, the viscosity of the fluid reverts to its original state. Magnetorheological fluids behave similarly in response to a magnetic field.

The changes in viscosity when electrorheological or magnetorheological fluids are exposed to electric or magnetic fields, respectively, can be startling. A liquid is seemingly transformed into a solid, and back again to a liquid as the field is turned off and on.

These phenomena are beginning to be utilized in a number of products. An electrorheological fluid embedded in an automobile tire, for example, can cause the stiffness of the tire to change upon demand; thus making it possible to 'tune' tires for better cornering or more comfortable straight riding. Some devices that typically require mechanical interfaces, e.g., clutches, might conceivably use smart rheological fluids as replacements for mechanical parts.

In architecture and industrial design, little use has been made of smart rheological fluids. One can imagine, however, chairs with smart rheological fluids embedded in seats and arms so that the relative hardness or softness of the seat could be electrically adjusted. The same is obviously true for beds.

LIQUID CRYSTAL TECHNOLOGIES

Liquid crystal displays are now ubiquitously used in a host of products. It would be hard to find someone in today's modern society that has not seen or used one. This widespread usage, however, does not mean that liquid crystal technologies are unsophisticated. Quite the contrary; they are a great success story in technological progress.

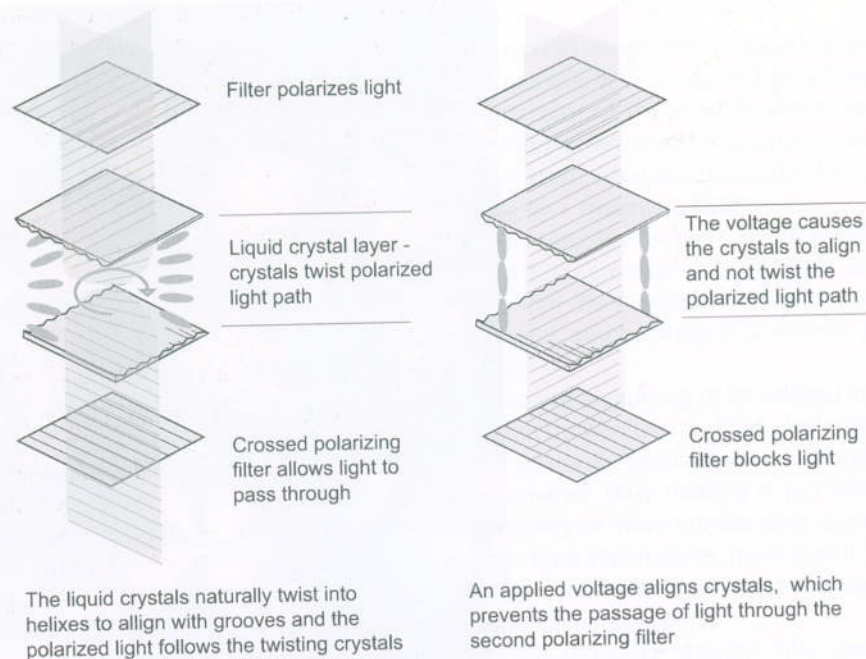
Liquid crystals are an intermediate phase between crystalline solids and isotropic liquids. They are orientationally ordered liquids with anisotropic properties that are sensitive to electrical fields, and therefore are particularly applicable for optical displays. Liquid crystal displays utilize two sheets of polarizing material with a liquid crystal solution between them. An electric current passed through the liquid causes the crystals to align so that light cannot pass through them. Each crystal is like a shutter, either allowing light to pass through or blocking the light.



▲ Figure 4-9 Progressive phase change of nematic liquid crystal films (the typical thermotropic liquid crystal similar to what is used in LCDs). (Images courtesy of Oleg D. Lavrentovich of the Liquid Crystal Institute, Kent State University)

No voltage - light transmitted

Voltage applied - light is blocked

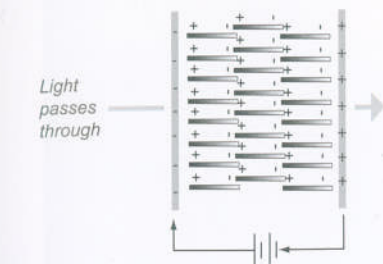
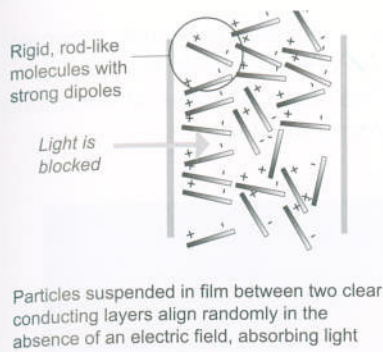


▲ **Figure 4-10** A liquid crystal display (LCD) uses two sheets of polarizing material and a liquid crystal solution sandwiched in between them

SUSPENDED PARTICLE DISPLAYS

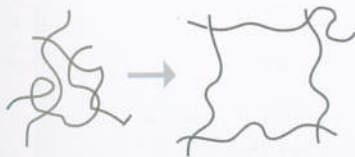
Newly developed suspended particle displays are attracting a lot of attention for both display systems and for more general uses. These displays are electrically activated and can change from an opaque to a clear color instantly and vice-versa. A typical suspended particle device consists of multiple layers of different materials. The active layer associated with color change has needle-shaped particles suspended in a liquid. (films have also been used). This active layer is sandwiched between two parallel conducting sheets. When no voltage is applied, the particles are randomly positioned and absorb light. An applied voltage causes the particles to align with the field. When aligned, light transmission is greatly increased through the composite layers.

Interestingly, the color or transparency level remains at the last setting when voltage was applied or turned off. A constant voltage need not be applied for the state to remain.



▲ Figure 4-11 Suspended particle display

Long chain molecular structures



Large reversible volume changes can occur due to changes in the surrounding environment.



Polyacrylamide polymer crystals with a strong affinity for water swell to several hundred times their size in water, and then can revert back to their original size on drying

▲ Figure 4-12 Volume-changing polymer gels

OTHER TYPE I MATERIALS

There are a great many other interesting materials that exhibit one form or another of property change. Shape-changing gels or crystals, for example, have the capacity to absorb huge amounts of water and in doing so increase their volumes by hundred-folds. Upon drying out, these same materials revert to their original sizes (albeit often in a deformed way). Applications are found in everything from dehumidification devices and packaging through to baby diapers and plant watering spikes.

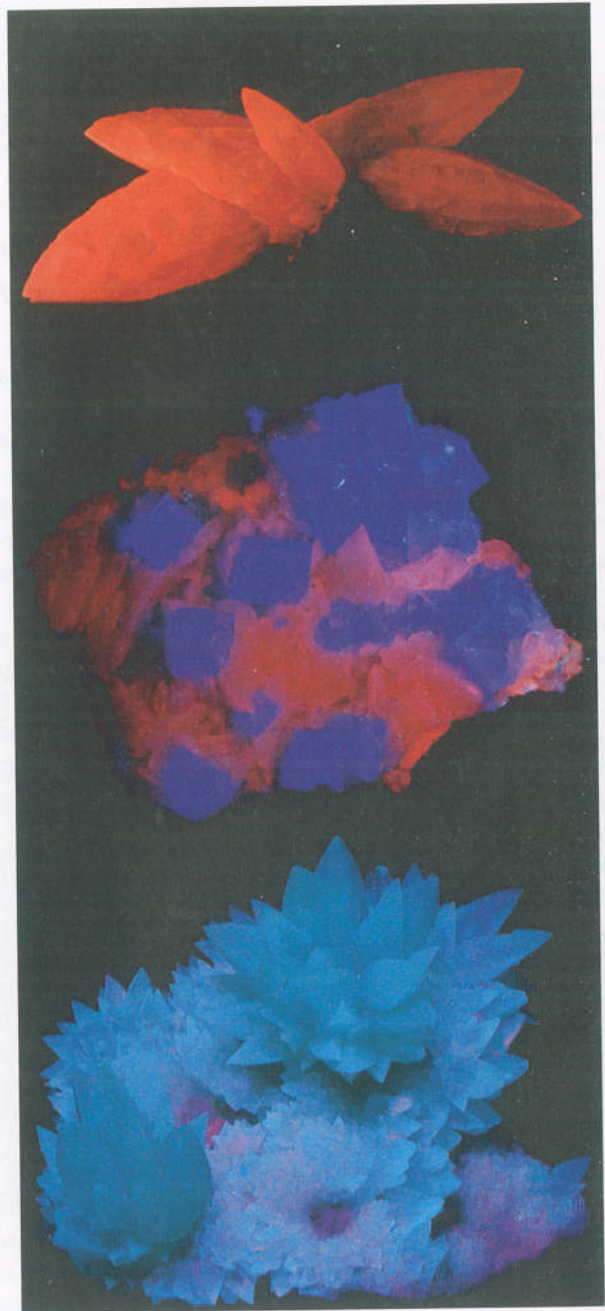
4.3 Type 2 smart materials – energy-exchanging

Energy fields – environments – surround all materials. When the energy state of a given material is equivalent to the energy state of its surrounding environment, then that material is said to be in equilibrium: no energy can be exchanged. If the material is at a different energy state, then a potential is set up which drives an energy exchange. All of the energy exchange materials involve atomic energy levels – the input energy raises the level, the output energy returns the level to its ground state. For example, when solar radiation strikes a photovoltaic material, the photon energy is absorbed, or more precisely – absorbed by the atoms of the material. As energy must be conserved, the excess energy in the atoms forces the atom to move to a higher energy level. Unable to sustain this level, the atom must release a corresponding amount of energy. By using semi-conductor materials, photovoltaics are able to capture this release of energy – thereby producing electricity. Note that all materials – traditional as well as smart – must conserve energy, and as such the energy level of the material will increase whenever energy is input or added. For most materials, however, this increase in energy manifests itself by increasing the internal energy of the material, most often in the form of heat. Energy exchange smart materials distinguish themselves in their ability to recover this internal energy in a more usable form.

Many of the energy-exchanging materials are also bi-directional – the input energy and output energy can be switched. The major exceptions to this are materials that exchange radiation energy – the high inefficiency of radiant energy exchange increases thermodynamic irreversibility. Furthermore, unlike most (although not all) of the property-changing materials, the energy-exchange materials are almost

always composite materials – exceptions include magnetostrictive iron and naturally occurring piezoelectric quartz.

The following sections describe a number of commonly used Type 2 energy-exchanging materials.



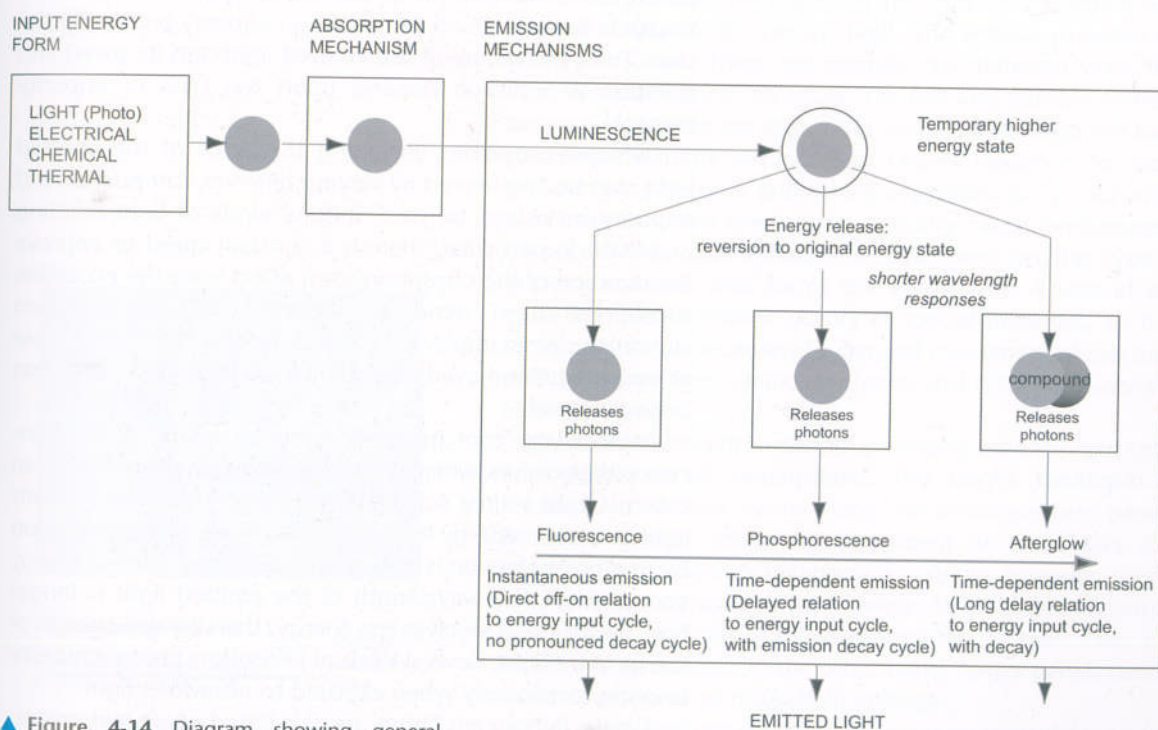
▲ **Figure 4-13** Three types of fluorescing calcite crystals (middle image also has fluorite mixed in) (Images courtesy of Tema Hecht and Maureen Verbeek)

LIGHT-EMITTING MATERIALS

Luminescence, fluorescence and phosphorescence

A definition of *luminescence* can be backed into by saying that it is emitted light that is not caused by incandescence,¹ but rather by some other means, such as chemical action. More precisely, the term luminescence generally refers to the emission of light due to incident energy. The light is caused by the re-emission of energy in wavelengths in the visible spectrum and is associated with the reversion of electrons from a higher energy state to a lower energy state. The phenomenon can be caused by a variety of excitation sources, including electrical, chemical reactions, or even friction. A classic example of a material that is luminescent due to a chemical action is the well-known 'light stick' used for emergency lighting or by children during Halloween.

Luminescence is the general term used to describe different phenomena based on emitted light. If the emission occurs more or less instantaneously, the term *fluorescent* is used. Fluorescents glow particularly brightly when bathed in a 'black light' (a light in the ultraviolet spectrum). If the



▲ Figure 4-14 Diagram showing general phenomenon of luminescence

emission is slower or delayed to several microseconds or milliseconds, the term *phosphorescence* is used. Many compounds are either naturally phosphorescent or designed to be so. The amount of delay time depends on the particular kind of phosphor used. Common phosphors include different metal sulfides (e.g., ZnS). Common television screens rely on the use of ZnS. Strontium aluminate is also strongly phosphorescent. In some situations, the light emission can continue long after the source of excitation is removed because the electrons become temporarily trapped because of material characteristics. Here the term *afterglow* is used.

Most materials that are luminescent are solids that contain small impurities, e.g., zinc sulfates with tiny amounts of copper. When these materials are exposed to incident energy in any of several forms, the energy associated with the impinging electrons or photons is absorbed by the material, which in turn causes electrons within the material to rise to a higher level. Following the descriptive model suggested by Flinn and Trojan, these electrons subsequently may fall into what are commonly called 'traps' associated with the impurities.² After a while, a trapped electron gains enough energy to leave its trap and in doing so produces a light photon in a wavelength in the visible spectrum. Its wavelength is dependent on the ion (e.g., copper) producing the trap. Thus, the nature of the emitted light and its speed and duration of emission depend upon the type of impurity present.

Different properties, including the color of the emitted light, can be engineered by varying different compounds and impurity inclusions to yield specific kinds of light-emitting materials. In particular, there is a constant quest to improve the duration of the phosphorescent effect once the excitation source has been removed. Materials such as strontium aluminate, for example, have been exploited for use because of their long afterglow duration once the excitation source has been removed.

Photoluminescence generally refers to a kind of luminescence that occurs when incident energy associated with an external light source acts upon a material that then re-emits light at a lower energy level. A process of electronic excitation by photon absorption is involved. As a consequence of energy conservation, the wavelength of the emitted light is longer (i.e., 'redder' and involves less energy) than the wavelength of the incident light. Several kinds of phosphors photoluminesce brightly, particularly when exposed to ultraviolet light.

Typical fluorescent lamps are also based on photoluminescent effects. The inside of a lamp is coated with a phosphor

that is excited by ultraviolet mercury radiation from a glow discharge.

In *chemoluminescence*, the excitation comes from a chemical action of one type or another. The lightstick mentioned earlier still provides the best common example of this phenomenon. Particularly interesting here is that chemoluminescence produces light without a corresponding heat output, which is surprising since a chemical reaction is involved. If the temperature of the surrounding heat environment is increased, however, there will be an increase in the reaction time, hence light output, and a reduction in temperature will correspondingly reduce the light output.

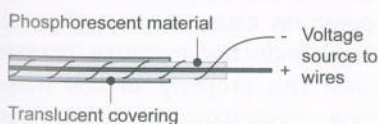
A subset of chemoluminescence normally called *bioluminescence* is particularly fascinating because it provides the glow associated with various light-emitting insects, such as fireflies, or fish such as the *Malacosteus*, which navigates the depths of the sea via its own night light. Consider, for example, the squid that can alter its luminescence to match either moonlight or sunlight.

Electroluminescence

With *electroluminescent* materials the source of excitation is an applied voltage or an electric field. The voltage provides the energy required. There are actually two different ways that electroluminescence can occur. The first and typical condition occurs when there are impurities scattered through the basic phosphor. A high electric field causes electrons to move through the phosphor and hit the impurities. Jumps occurring in connection with the ionized impurity cause luminescence to occur. The color emitted is dependent on the type of impurity material that forms the active ions. A second and more complex behavior occurs in special materials, such as semiconductors, because of a general movement of electrons and holes (see *Semiconductors, Lasers and LEDS (light-emitting diodes)* below).

Electroluminescent materials are widely used for light strips and panels of all descriptions. The bright backlights in inexpensive watches are invariably electroluminescent panels. As noted above, colors are dependent on the active ions selected for use. In very inexpensive systems, however, simple colored filters are used to give variety. Strips or panels can be designed to work off of different applied voltages. They can be battery operated. On the other hand, larger panels can be made to respond to household voltages.

Since the luminescent effect depends on phosphors and an electric field, electroluminescent strips or panels can be made



▲ Figure 4-15 Electroluminescent wire



▲ Figure 4-16 Electroluminescent strips

using a variety of different neutral substrates. Very simple strips can be made in which a phosphorous material is applied evenly to a polymeric strip, and covered by another transparent strip for protection. A small wire to provide the electric field is applied to the strip. Voltage sources can be batteries. Larger panels can be made using polymeric materials as well. An electric strip would essentially surround the panel. Interestingly, these polymeric panels can literally be cut into different shapes as long as the electrical field can be maintained. Other materials that are often used as substrates include glass, ceramics and plastics.

Electroluminescent lamps are becoming widely used. They draw little power and generate no heat. They provide a uniformly illuminated surface that appears equally bright from all angles. Since they do not have moving or delicate parts, they do not break easily. Chapter 6 discusses applications in more detail.

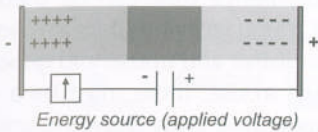
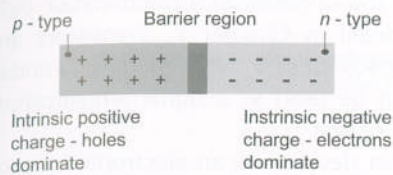
BASIC SEMICONDUCTOR PHENOMENA

Few people have not heard of *semiconductors* – the materials that have helped usher in an age of high-powered microelectronic devices. The basic phenomenon underlying a semiconductor forms the basis for other technologies as well, including transistors and, of special interest in this book, the photovoltaic effect associated with solar power. Few people, of course, have any idea of what this phenomenon actually involves and what semiconducting devices actually do. Here we will only touch on the salient features of these complex materials.

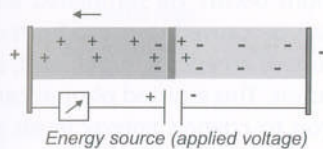
Basic semiconductor materials, such as silicon, are neither good conductors nor good insulators, but, with the addition of small impurities called *dopants*, they can be made to possess many fascinating electrical properties. The addition of these dopants or impurities allows electron movements to be precisely controlled. Exploitation of the resultant properties has allowed a semiconductor to serve the same functions as complicated multipart electronic circuitries.

Silicon is the most widely used semiconducting material, although other material types are possible. Basic semiconducting materials exhibit interesting properties when surrounding temperatures are varied. Unlike most metals wherein increases in temperatures cause increases in resistance, the conductivity of semiconducting materials increases with increasing temperatures. This property already makes it quite attractive for many applications. It results from a particular type of electron band structure in the internal

Semiconductor materials with different added selected impurities (*dopants*) - conductivities increase with temperatures in semiconductor materials



In the reverse bias mode, there is no flow of current across the barrier region



In the forward bias mode, the current increases exponentially with the applied voltage

▲ Figure 4-17 Basic semiconductor behavior

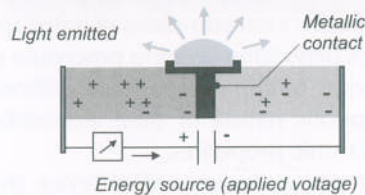
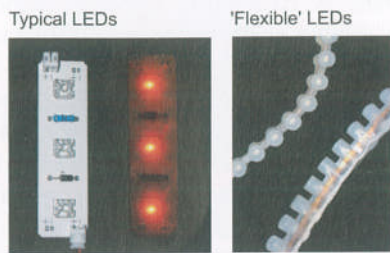
structure of the materials. A gap exists between bands through which thermally excited electrons cross in particular conditions.

The addition of dopants or impurities creates other conditions. The role of impurities with respect to light-emitting materials was previously noted. Of importance in this discussion is the role of the impurities in affecting the flow of electrons through a material. Here again the flow is affected, but in this case in a controllable way. Silicon matrix materials are alloyed with specific concentrations of a dopant, such as boron, via a complex deposition layering procedure to form a semiconductive device. Multiple dopants of different types may be used. The specific nature of these assemblies determines their useful electronic properties.

Figure 4-17 illustrates a typical makeup of a device that consists of a junction of so-called *p* and *n* semiconductor materials (made by using different dopants on silicon substrates). In the first type of material, *n*, electrons with a negative charge are predominantly present. In the second type, *p*, holes (locations of missing electrons) are primarily present resulting in a positive charge. Application of a negative charge to the *p* side causes the charges to be electrostatically attracted away from each other, creating a zone that is free of electrons. No current flows through this region. Application of a positive charge to the *p* side causes the reverse situation. Electrons flow through the barrier zone creating a current.

PHOTOVOLTAICS, LEDS, TRANSISTORS, THERMOELECTRICS

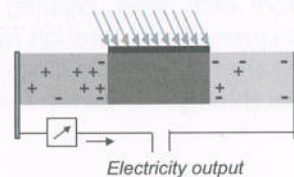
Many widely used devices have their fundamental basis in semiconductor technology. *Photovoltaic* technologies are discussed in detail elsewhere (see Chapter 7). Here it is important to note that the basic underlying phenomenon is related to the semiconductor behavior noted above. A photovoltaic device consists primarily of a *p* and *n* junction. Instead of there being an applied voltage as described above, however, there is an incident energy (typically solar) that acts on the junction and provides the external energy input. In typical solar cells, the *n* layer is formed on top of the *p* layer. Incident energy impinges on the *n* layer. This incident energy causes a change in electron levels that in turn causes adjacent electrons to move because of electrostatic forces. This movement of electrons produces a current flow. Phototransistors are similar in that they convert radiant energy from light into a current.



In a light-emitting diode (LED), energy input into the junction creates a voltage output

▲ **Figure 4-18** Light emitting diodes (LED) are based on semiconductor technologies

Energy source - radiant energy from light



a photovoltaic device (solar cell), energy put into the junction creates a voltage output

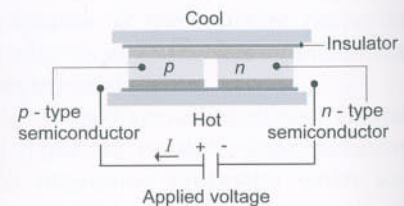
▲ **Figure 4-19** Photovoltaic (PV) devices are based on semiconductor technologies

Common LEDs (*light-emitting diodes*) are based essentially on the converse of photovoltaic effects. An LED is a semiconductor that luminesces when a current passes through it. It is basically the opposite of a photovoltaic cell. LEDs are discussed in detail in Chapter 7. Transistors are similarly based on semiconductor technologies. Fundamentally, a transistor can be used as a signal amplification device, or as a switching device.

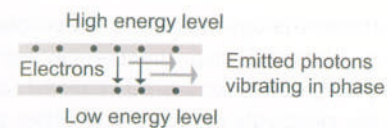
Thermoelectrics or *Peltier* devices are an electronic form of heat pump. A typical Peltier device uses a voltage input to create hot and cold junctions, hence they can be used for heating or cooling. They are found in computers as cooling devices, and in common automotive and household goods as small heaters or coolers. When in use, there must be a way provided to carry the heat generated away from the unit. In larger units, fans are commonly used.

Lasers are one of the ubiquitous workhorses of today's technological society. Laser light occurs via stimulated emission. In a laser, an electron can be caused to move from one energy state to another because of an energy input, and, as a consequence, emit a light photon. This emitted photon can in turn stimulate another electron to change energy levels and emit another photon that vibrates in phase with the first. The chain builds up quickly with increasing intensity. Emitted photons vibrate in phase with one another. Hence the light is phase-coherent. The term 'coherent light' is often used. The light is monochromatic, which in turn allows it to be highly focused. Since the light occurs via stimulated emissions, the acronym Laser was adopted (i.e., light amplification by stimulated emission of radiation).

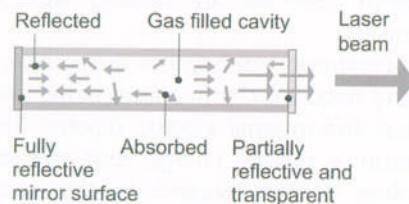
Many types of lasers exist that rely on different methods of excitation and use different materials. There are ruby lasers,



▲ **Figure 4-20** In a Peltier device an input electrical current causes one face to heat up and the other to cool down. Ceramic plates are used in the device shown. It is necessary to transfer heat away from the hot surface via fans or heat spreaders. Peltier devices are used in many products, including drink coolers and in computers to cool microchips

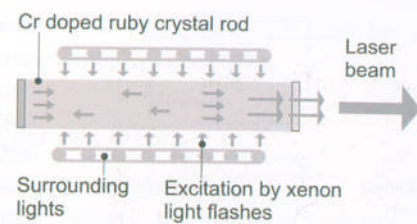


Basic principles - light amplification by stimulated emission of radiation (LASER)

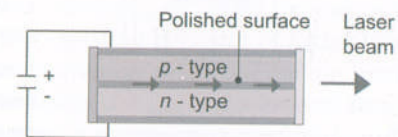


Gas lasers - photon are bounced back and forth with increasing intensity to create a high powered laser

▲ Figure 4-21 Lasers – basic principles and types



Ruby crystal laser - photons are excited by flashes from surrounding xenon lights



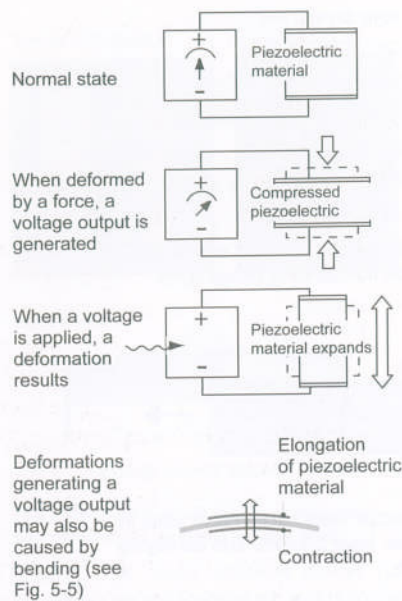
'Semiconductor' laser - commonly used in laser guides, laser printers, and surveying equipment

gas lasers and so forth. Powers can vary. Gas lasers can be quite powerful and cut many materials. The most ubiquitous kind of lasers used in printers, pointers, construction levels, surveying instruments etc. are typically based on semiconductor technologies (see Figure 4-21).

PIEZOELECTRIC EFFECTS AND MATERIALS

In this section we enter into the world of the *piezoelectric effect* that forms the underlying basis for products as diverse as some types of microphones and speakers, charcoal grill fire starters, vibration reducing skis, doorbell pushers and an endless number of position sensors and small actuators. All of these devices involve use of a piezoelectric material in which an applied mechanical force produces a deformation that in turn produces an electric voltage, or, conversely, an applied voltage that causes a mechanical deformation in the material that can be used to produce a force. This general phenomenon is called the piezoelectric effect.

The *piezoelectric phenomenon* (piezo means pressure in Greek) was observed by the brothers Pierre and Jacques Curie when they were 21 and 24 years old in 1880. They observed that when a pressure is applied to a polarized crystal, the mechanical deformation induced resulted in an electrical



▲ Figure 4-22 Piezoelectric behavior

charge. The phenomenon is based upon a reversible energy conversion between electrical and mechanical forms that occurs naturally in permanently polarized materials in which parts of molecules are positively charged and other parts are negatively charged. Many naturally found crystals (e.g., quartz) possess this property, as do many newly developed polymers and ceramics. The property is curiously similar to that found in magnets where permanent magnetic polarization occurs, except here we are dealing with electrical charges.

In piezoelectric materials, each cell or molecule is a dipole with a positive and negative charges onto either end. There is an alignment of the internal electric dipoles. This alignment can result in a surface charge, but this charge is neutralized by free charges present in the surrounding atmosphere. A force is applied to the piezoelectric material that causes deformations to take place, which in turn alters the neutralized state of the surface by changing the orientation of the dipoles. The reverse can also be achieved. Applying a voltage causes polarized molecules to align themselves with the electric field, which, in turn, causes a deformation to develop.

The piezoelectric effect has long been exploited in many different devices. The obviously desirable property wherein a pressure produces a voltage is used in many different ways. In the common doorbell pusher, an applied force produces a voltage, which in turn is used to control an electrical circuit causing the irritating chime or delightful buzz. In the previously mentioned charcoal lighter, application of a force to a piezoelectric device causes an ignition spark. Less obvious to most people, but more widely used, are a whole host of piezo-based devices that serve as small electrically controlled actuators used in a variety of mechanical and industrial situations wherein a small voltage causes a part movement that controls something else, such as a valve.

The piezoelectric effect is literally instantaneous and piezoelectric devices can be quite sensitive to small pressures or voltages. Many microphones based on piezoelectric materials transform an acoustical pressure into a voltage. Alternatively, in piezoelectric speakers, application of an electrical charge causes a mechanical deformation, which can in turn create an acoustical pressure.

Uses can be surprising. Piezoelectric materials have been used in skis to damp out undesirable vibrations that can occur under certain conditions. Here, the piezoelectric effect dampens vibrations by dissipating the electrical energy developed across a shunting. Other situations involving

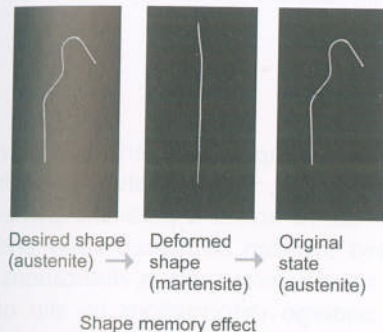
vibratory movements in many products can be selectively damped out using similar technologies.

SHAPE MEMORY ALLOYS

Perhaps surprisingly, eyeglass frames that are amazingly bendable, medical stents for opening arteries that are implanted in a compressed form and then expand to the right size and shape when warmed by the body, tiny actuators that eject disks from laptop computers, small microvalves and a host of other devices, all share a common material technology. The interesting behavior of each of these devices relies upon a phenomenon called the 'shape memory effect' that refers to the ability of a particular kind of alloy material to revert, or remember, a previously memorized or preset shape. The characteristic derives from the phase-transformation characteristics of the material. A solid state phase change – a molecular rearrangement – occurs in the shape memory alloy that is temperature-dependent and reversible. For example, the material can be shaped into one configuration at a high temperature, deformed dramatically while at a low temperature, and then revert back to its original shape upon the application of heat in any form, including by an electrical current. The phenomenon of superelasticity – the ability of a material to undergo enormous elastic or reversible deformations – is also related to the shape memory effect.

Nickel–titanium (NiTi) alloys are commonly used in shape memory applications, although many other kinds of alloys also exhibit shape memory effects. These alloys can exist in final product form in two different temperature-dependent crystalline states or phases. The primary and higher temperature phase is called the austenite state. The lower temperature phase is called the martensite state. The physical properties of the material in the austenite and martensite phases are quite different. The material in the austenite state is strong and hard, while it is soft and ductile in the martensite phase. The austenite crystal structure is a simple body-centered cubic structure, while martensite has a more complex rhombic structure.

With respect to its stress–strain curve, the higher temperature austenite behaves similarly to most metals. The stress–strain curve of the lower temperature martensitic structure, however, almost looks like that of an elastomer in that it has 'plateau' stress-deformation characteristics where large deformations can easily occur with little force. In this state, it behaves like pure tin, which can (within limits) be bent back and forth repeatedly without strain hardening that can lead to

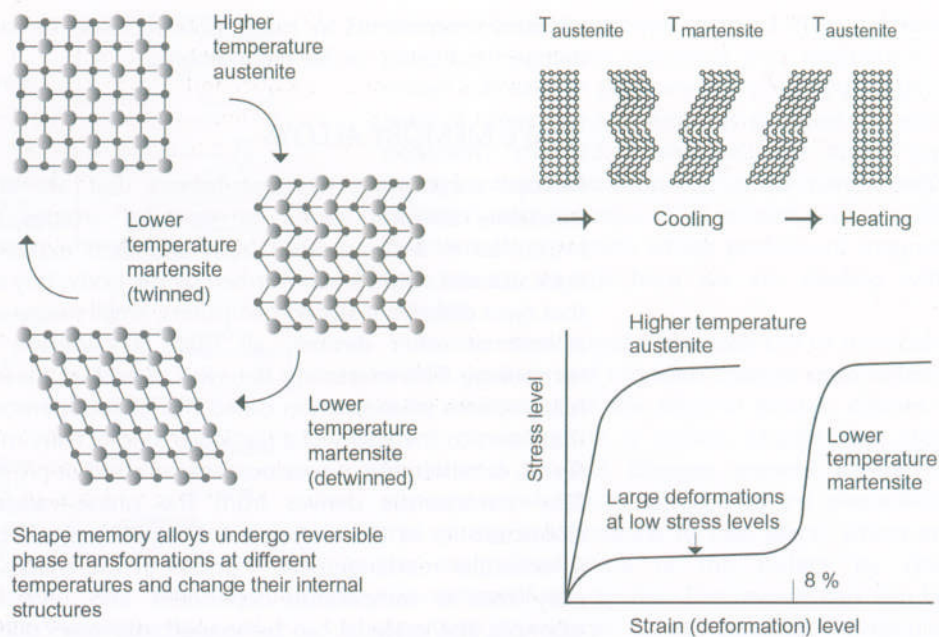


Material is given a shape while in the higher temperature austenite phase

While in the lower temperature martensite phase, the material can be easily deformed into another shape

Upon the application of heat, the material returns to its higher temperature austenite phase and to its original shape

▲ **Figure 4-23** In a thermally induced shape memory effect, a material can be deformed, but 'remembers' its original shape after heating. Shape memory effects may also be induced in other materials by magnetic fields



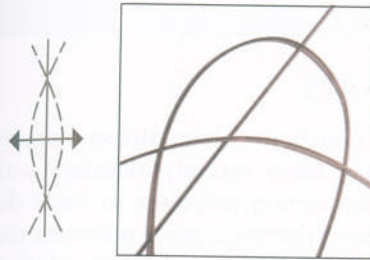
▲ **Figure 4-24** – Shape memory alloys (e.g., Nitinol) that exhibit thermally induced shape memory effects

failure. The material in the lower temperature martensite state has a 'twinned' crystalline structure, which involves a mirror symmetry displacement of atoms across a particular plane. Twin boundaries are formed that can be moved easily and without the formation of microdefects such as dislocations. Unlike most metals that undergo deformations by slip or dislocation movement, deformation in a twinned structure occurs by large changes in the orientation of its whole crystalline structure associated with movements of its twin boundaries.

The thermally induced shape memory effect is associated with these different phases. In the primary high temperature environment, the material is in the austenite phase. Upon cooling the material becomes martensitic. No obvious shape change occurs upon cooling, but now the material can be mechanically deformed. It will remain deformed while it is cool. Upon heating, the austenitic structure again appears and the material returns to its initial shape.

A related mechanically induced phenomenon called *superelasticity* can also take place. The application of a stress to a shape memory alloy being deformed induces a phase transformation from the austenite phase to the martensite

The shape memory alloy changes from an austenite phase to a martensite phase during deformation.



▲ Figure 4-25 Superelasticity – a mechanically induced shape memory effect

phase (which is highly deformable). The stress causes martensite to form at temperatures higher than previously and there is high ductility associated with the martensite. The associated strains or deformations are reversible when the applied stress level is removed and the material reverts back to austenite. High deformations, on the order of 5–8%, can be achieved. Changes in the external temperature environment are not necessary for the superelasticity phenomenon to occur.

Why these phenomena occur is fundamentally a result of the need for a crystal lattice structure to accommodate to the minimum energy state for a given temperature. There are many different configurations that a crystal lattice structure can assume in the martensite phase, but there is only one possible configuration or orientation in the austenite state, and all martensitic configurations must ultimately revert to that single shape and structure upon heating past a critical phase transition temperature. The process described is repeatable as long as limits associated with the transition phases are maintained. Under high stress or deformation levels, a form of fatigue failure can occur after repeated cycles.

Both of the two primary phenomena associated with shape memory effects – thermally induced effects and mechanically induced effects – have direct applications. In the shape memory effect associated with the thermal environment, a material having an initial shape while in its high temperature austenite phase can subsequently be deformed while in a lower temperature phase martensite phase. When reheated to the high temperature austenite phase by a heat stimulus, such as an electric current (but any heat source will work), the alloy reverts back to its initial shape. During this process, a high force is generated by the phase-changing material. The material can thus be used as an actuator in many different applications. Usually the material provides the primary force or actuating movement as part of a larger device. Since the force and movement occur within the material itself, devices using it are often very simple as compared to more traditional mechanical actuators. Heat in the form of electrical current is easy to apply and electronically control. Hence, the widespread use of shape memory alloys in release latches and a host of other devices.

In the shape memory effect associated with the mechanical environment, or superelasticity, the material can undergo an elastic deformation (caused by an external force) that can be as high as twenty or more times the elastic strain of normal steel. Superelastic materials thus exhibit incredible abilities to deform and still 'spring back' to their original shape. An initial

consumer application of superelastic materials was in eye-glass frames that could seemingly be tied in knots, but which reverted to their original shape upon release.

SHAPE MEMORY POLYMERS

Alloys are not the only materials to exhibit shape memory effects. A major effort has been recently directed with considerable success to engineering polymers to have the same effects. Applications are enormous, since polymers can be easily fabricated in a number of different forms. Medical applications, for example, include the development of shape memory polymeric strands to be used in surgical operations as self-tying knots. The strands are used to tie off blood vessels. The strands are given an initial shape, looped around a vessel and, as the body heat operates on the polymer, the strand ties itself into a knot (its remembered shape).

Notes and references

- 1 Incandescent light is generated by the glowing of a material due to high temperatures, i.e., it is emitted visible radiation associated with a hot body.
- 2 Flinn, Richard and Trojan, Paul (1986) *Engineering Materials and Their Applications*. Boston, MA: Houghton Mifflin.