

# Glass in class

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## Abstract

Glass is reviewed from fabrication to application, laying emphasis on the wide-ranging physics involved. This begins with liquids and solids and the way in which glasses are defined and can be demonstrated in the classroom. At the atomic level the regular structure of crystals and their irregular counterparts in glasses are explained through easy-to-teach toy models. A future article will describe applications of glasses from optical fibres to self-cleaning windows. The intention throughout is to emphasize the rich resource that glass can provide in class for teaching physics holistically.

 This article features online multimedia enhancements

## Glass and physics

Glass is a classic material for teaching physics, because it brings together so many different facets of the subject, from the distinctions between fluids and elastic media to the quantum mechanics of condensed matter. Where would optics be without glass lenses and prisms, astronomy without glass mirrors, x-rays without glass vacuum tubes? In applied physics how could integrated circuits have been developed without the crucial nanometre of silica glass, liquid crystal displays without those perfectly parallel thin glass plates, broadband telecommunications without the incredibly low optical loss achievable in glass fibres? Glass is everywhere in modern life.

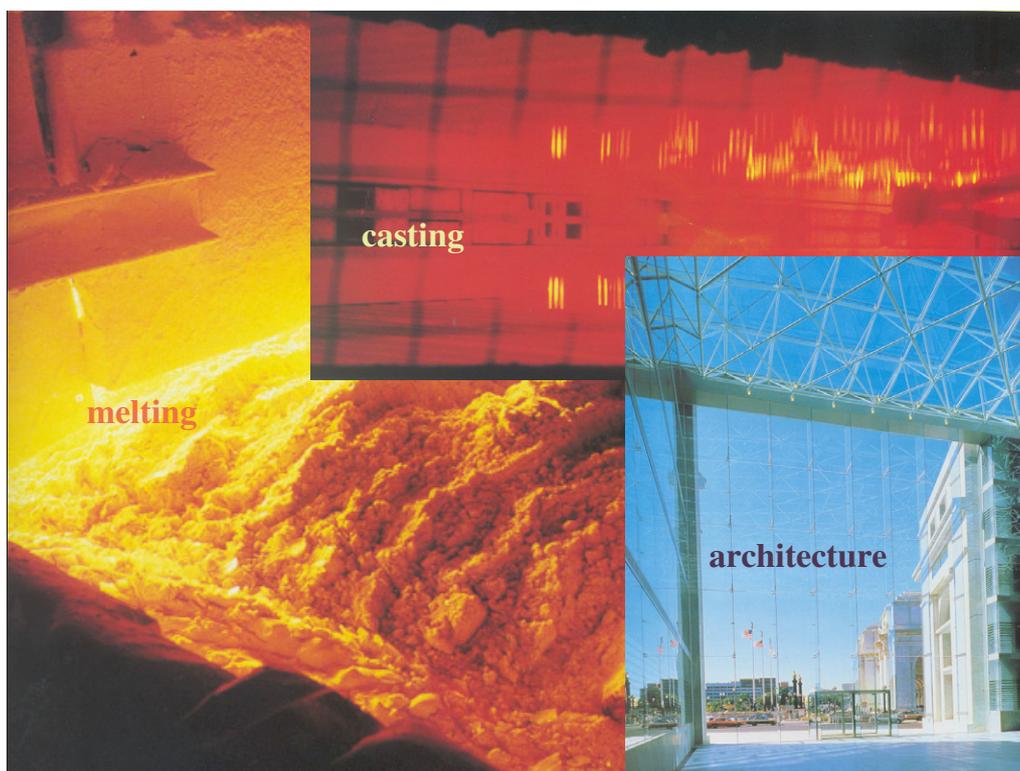
It is the traditional applications of glass, though, that make it such a rich source of cues to capture attention: windows, architecture, thermal insulation, glassware, light bulbs, VDU screens, camera objectives and so on. At the same time, with modern fabrication methods, the glassy state now extends to polymers, biogenic glasses, amorphous semiconductors, metals and magnetic materials—extending the list of applications still further. Indeed in the last 20 years glass has become the alternative to the crystalline state in condensed matter, and because of that it offers

many new opportunities for learning and teaching physics.

Curiously one of the reasons glass is still considered an esoteric material is because solid state physics is traditionally grounded on periodic wave functions (Bloch waves) and objects in reciprocal space like Brillouin zones and Fermi surfaces. Understanding amorphous materials, however, requires none of these erudite constructions. Indeed the glassy state provides excellent examples of how to approach complexity, with new physics and new empiricism, combining multiple experimental probes drawn together through computer modelling. This review and a subsequent article on applications in glass will attempt to provide some prime examples of how glass can be used as a source of consolidation in teaching physics and also as a platform for introducing new ideas. Each section ends with a brief summary (in *italics*). The illustrations with animation are available as a Powerpoint file from the electronic version of this journal.

## Glass from start to finish

History is a wonderful thing, particularly the evolution of technology. Starting from the popular



**Figure 1.** Glass from start to finish.

conception that glass is a frozen liquid, what the Phoenicians (reputedly) stumbled on, whilst raking through the dying embers of beach fires, was the residue from a liquid that had become too viscous to crystallize as the temperature dropped—bright beads like jewels. Indeed this was the original application of glass. Attention then turned to ornaments when the first ingots were successfully fabricated by wrapping soft glass around friable cores. These articles were often reserved for burial but, as the technology advanced and bowls formed by slumping molten sheet over hemispheres were created, glass entered the houses of the living. In the meantime, as clear glass was developed, this led to the production of glass in pure colours, adaptable for glazes. Then the Romans discovered glass blowing, glassware became affordable and designed for obsolescence, but with the occasional masterpiece created to be cherished rather than used.

Mediaeval alchemists rediscovered the Roman secrets of delivering the primary colours and stained glass entered ecclesiastical architecture with the arrival of gothic cathedrals. From

church to state, once reasonable security was established, windows became the secular interface between the house and the land that was owned. Initially widows were inordinately expensive, but when the sheet glass process was invented in the 19th century, this ushered in the continuous mass production of fire-finished glass, and windows became affordable to almost everyone. Following sheet glass production, Pilkington developed on-line polishing—a mammoth process—that reduced the cost of plate glass for large windows and mirrors. Finally, in the mid 20th century, when the float glass process arrived—casting glass on molten tin—the material to be looked through rather than gazed at became the prolific material we know today. The only downside is the huge energy cost: 90% of the final price; for glass, like steel, is made under extreme conditions. Yet the process depicted in figure 1, of taking crystals of sand, soda and lime plus some crushed glass to make a clear liquid at 1500 °C, and then casting and annealing it to make still more glass, non-crystalline and transparent, remains virtually unchanged throughout five millennia.

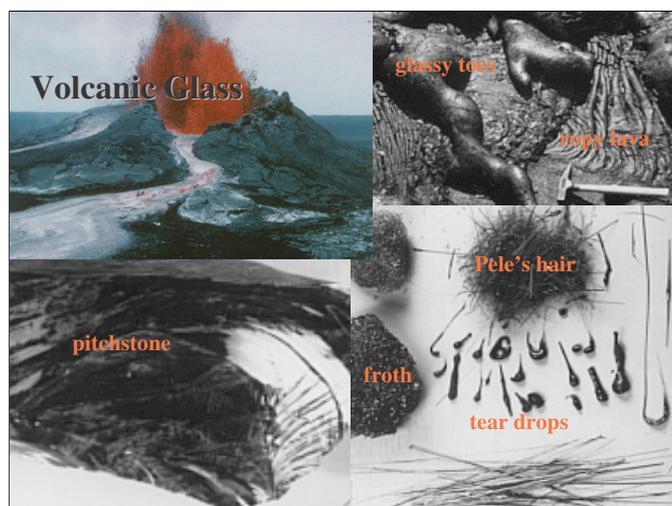


Figure 2. Various types of glass.

Another irresistible line to take in capturing interest in glass is to take the example of basaltic glass, the debris of volcanic activity. Similar in composition to manufactured glass, it is also cast at similar temperatures but usually quenched more abruptly! Like artificial glass, it forms fibres, drops and sometimes huge chunks of dark green cullet, heavy in iron impurities. The Natural History Museum in London has masses of this. Pictures, though, are very impressive in themselves (figure 2). Perhaps the most convincing way to convey the phenomenon of glass formation, however, is to cast glass in front of pupils—‘glass in class’. Yet it is true that the advent of risk assessment now virtually precludes the pouring of white-hot liquid onto a copper plate with the risk of shattering the hot vitreous product into people’s faces. Too many goggles and screens, though, rather kill the drama. There are, however, more benign alternatives, like ladling molten boiled sweets from a hot pan onto a baking tin or quenching treacle onto ice packs. The closer you get to handling polysaccharides, though, the more messy the aftermath. At any rate, obsidian shapes like Pele’s hair and glass toes (figure 2) can be created in the classroom, if only temporarily.

*The point about the history of technology is that it records success not failure. It is confidence-building and it remains a brilliant lead-in to the commonwealth of science, with physics close to centre stage. Geophysics too has a special resonance, particularly today wherever*

*technology can be seen to replicate extreme conditions safely.*

### Liquids and solids

The physical differences between the liquid and the solid state are so striking that they can become counterintuitive in considering glass. If glass is a frozen liquid, what attributes of either state does it acquire? There are two main differences between fluids and solids, of which the most well-known is the response to shear. Solids distort elastically; liquids and fluids just flow, and cease to flow when the stress is removed. Figure 3 brings this contrasting behaviour together. Shear stress  $\sigma$  is always the same,  $F/A$ , but with solids the strain,  $\gamma$ , or distortion angle,  $x/z$ , is fixed, whereas with liquids it is dynamic,  $d\gamma/dt$ , and usually expressed as a velocity gradient,  $v_x/z$ . Leaves on water travel whilst those on the bed of the stream don’t go far.

The law of elastic shear for solids and Newton’s law of viscosity for classical liquids are linear. The respective proportionality constants, the elastic shear modulus,  $G$ , and viscosity,  $\eta$ , are well catalogued for most common materials and offer a quality check that physics is being sensible. So in table 1, diamond is obviously the most rigid and polyethylene the least, whilst silica glass is intermediate. Turning to viscosity, blood is clearly thicker than water (at the same temperature) and glycerine at 0 °C has the same consistency as molten glass at 1000 °C. To state the obvious, solids remain rigid until they melt whilst liquids

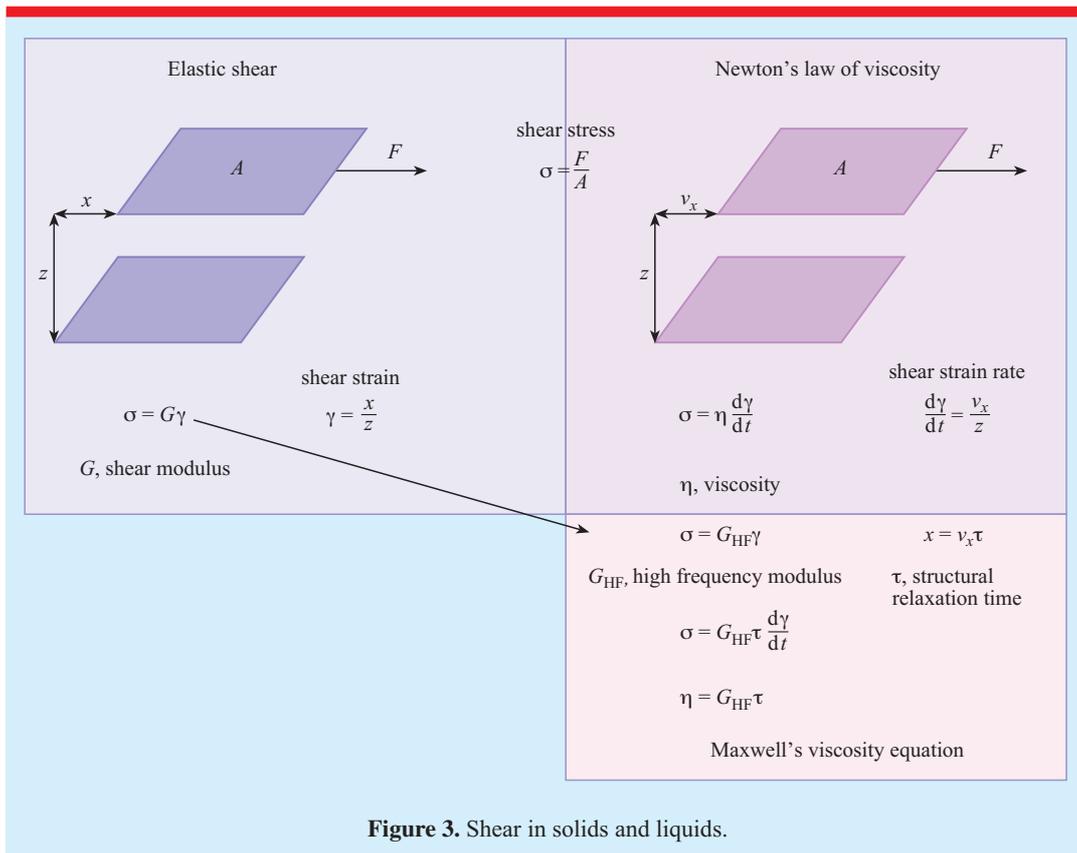


Figure 3. Shear in solids and liquids.

become more viscous as the temperature falls. Glass formation offers a dramatic example of this progression, where the viscosity drops through 22 decades between the molten state and room temperature (figure 4). Approximately halfway along (logarithmically) is a 'golden viscosity figure' of  $10^{12}$  Pa s where before our eyes the liquid state appears to cease and the solid state take over—the *glass transition*. For window glass the temperature where this happens is just short of  $500^\circ\text{C}$ —dull red heat. Other significant points are the *flow point* at  $10^4$  Pa s and  $900^\circ\text{C}$ , the temperature of the white hot gob that the glass-blower works and fashions, and the *strain point* at  $10^{14}$  Pa s, where glass may crack if it is not properly annealed.

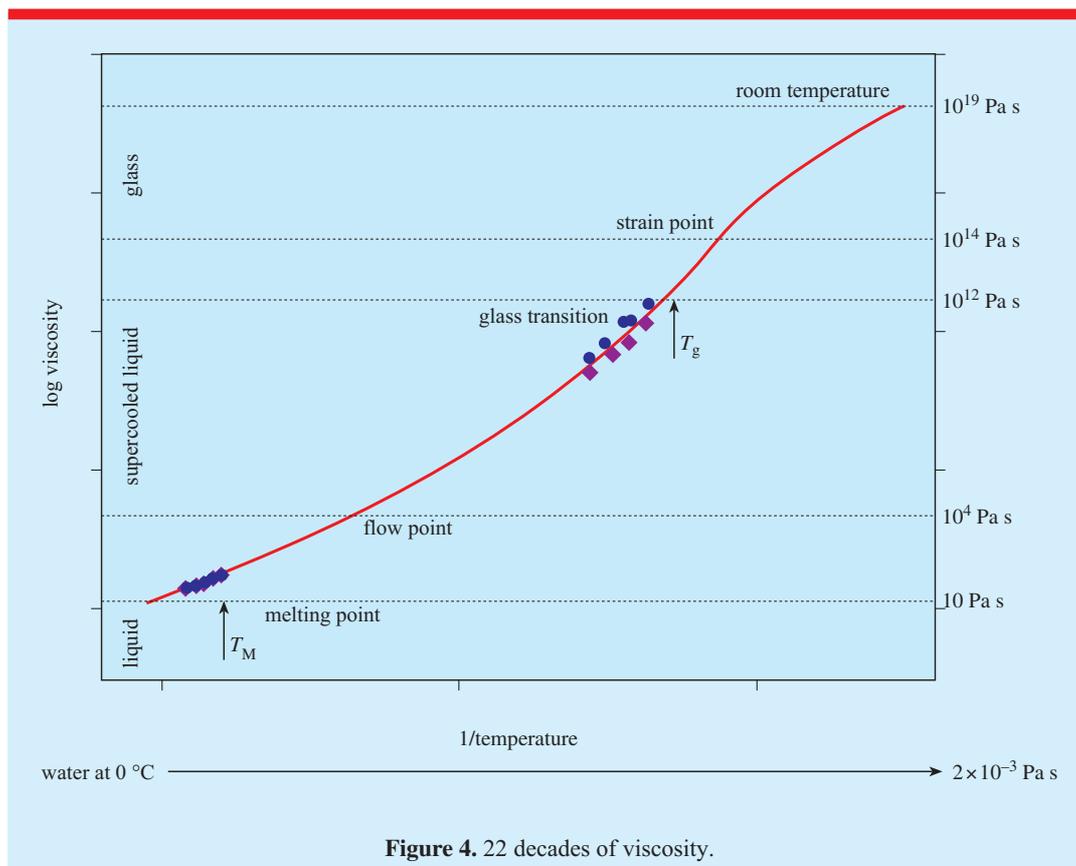
There is an important connection between the response of solids and liquids to shear, which is embodied in one of those equations attributed to Maxwell (figure 3). Not so famous as his equations of electromagnetism, this fundamental law of fluid dynamics puts the glass transition onto a time frame that makes sense of the dichotomy

between the liquid and the solid state. There are two extreme contributions to the response of a liquid or fluid to shear. The first draws on the observation that the initial reaction of liquids to shear stress is very similar to that of solids. It defines an instantaneous or high-frequency shear modulus,  $G_{HF}$ , which experimentally is not dissimilar in value to the shear modulus,  $G$ , of the corresponding solid. The first stroke of the oar feels like solid resistance. At the other extreme, Maxwell conjured up a structural relaxation time,  $\tau$ , that was fixed for a given viscosity. This defines a value for the displacement,  $x (= v_x\tau)$ , as a result of which the viscosity can be expressed as  $\eta = G_{HF}\tau$ . There are some subtleties missing from the simple account illustrated in figure 3, but put simply it helps to square elastic with viscous behaviour.

Armed with  $\eta = G_{HF}\tau$  and the experimental value of 25 GPa for  $G_{HF}$  for glass, all the viscosities in figure 4 can be re-expressed in 22 decades of structural relaxation time. Importantly, the structural relaxation time at the glass transition

**Table 1.** Shear moduli and viscosities for well-known solids and liquids.

Solids	Shear modulus $G$ (GPa)	Liquids	Viscosity $\eta$ (Pa s)
Diamond	430	Glass transition	$10^{12}$
Iron	111	Glass flow point	$10^4$
Silicon	79.6	Molten glass	10
Glass	31.2	Glycerine (0 °C)	10
NaCl	12.8	Blood (37 °C)	0.004
Polyethylene	0.04	Water (37 °C)	0.0008



**Figure 4.** 22 decades of viscosity.

is just short of a minute. This is our typical attention span and is taken as the timescale of glass formation. It reflects the point at which the liquid state appears at a glance to have become frozen. On a longer timescale the glass transition occurs at higher viscosities and vice versa. The choice of  $10^{12}$  Pa s is just practical. At the other extremes in figure 4, the structural relaxation time of molten glass is 40 ps—a decade longer than the period of the slowest atomic oscillations. It is also the timescale of many computer simulation experiments. By room temperature, on the other

hand, the structural relaxation time has extended to around ten years. This strengthens the view that glass might flow over time and worries the telecom industry, which is concerned about retaining limits on the geometry of optical fibres that guarantee their performance many years on.

*Whilst the physics of solids and liquids is comparatively easy to bring together on paper, it is pretty conceptual and a difficult learning and teaching experience. Nevertheless the rewards are the killing of several birds with one stone, the opportunity for demonstrations and raising the*

popular question about whether glass distorts over the centuries or not.

### Order or disorder

The other important physical difference between liquids and solids relates to atomic structure, namely how ordered or disordered atomic arrangements come about. There is a common misconception that crystalline materials are perfect and glasses are a complete mess. On the contrary, glasses are usually far closer to perfection than their crystalline cousins in terms of defects like broken bonds and missing atoms; it's just that the atomic structure of glass lacks periodicity, which has become a mantra for perfection. Blame the higher education sector and textbooks on solid state physics for that.

At the level of the forces between atoms, though, glasses and crystals have to be almost indistinguishable because they comprise the same atoms with the same starting electronic configurations. The classical Lennard-Jones potential that defines these forces is outlined in figure 5. Like all other interatomic potentials for metals, semiconductors and so on, this is made up of an attractive part that is electrostatic in origin (representing van der Waals forces in this case) and a repulsive part that is the hard-core repulsion of atoms whose electrons resist occupying the same space as their neighbours. Bound up in the Paul Exclusion Principle, electrons on adjacent atoms residing in identical quantum mechanical states cannot superimpose. The compromise between repulsion and attraction is the asymmetric potential well illustrated in figure 5. The minimum,  $dU/dr = 0$ , defines the interatomic separation,  $r_0$ , at the lowest temperatures and the asymmetry the thermal expansion as the temperature rises,  $dr_0/dT$ . The reader is also referred to the article by Bourg (2004), where the Lennard-Jones potential was mentioned in terms of interactions between agents in computer games: poles apart but similar physics!

Getting back to atoms, the geometry they adopt locally in a solid is tied to the interatomic potential, and that is almost independent of whether the long-range order is periodic or not. Indeed, potentials like the one in figure 5 can be used for realistic computer simulation of liquids as well as glasses (to be discussed later) or indeed crystals. The principal global difference between

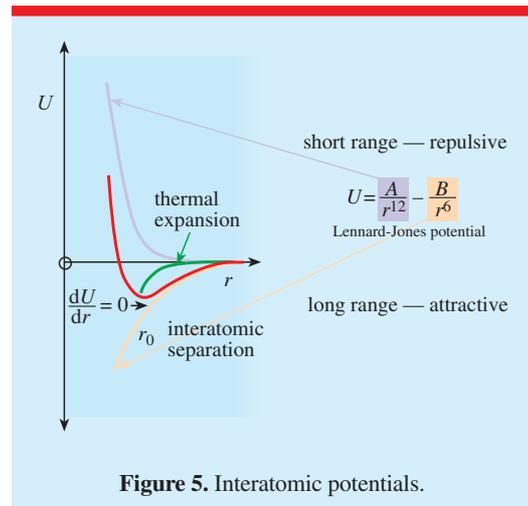


Figure 5. Interatomic potentials.

crystals and glasses lies in the total energy of the ensemble, for which entropy is the main distinction. The structure of a disordered solid encompasses numerous different configurations, like the frozen animation of footballers in a soccer photograph. The net result is that glasses have a higher internal energy than crystals of the same composition. In terms of energy, then, glasses are unstable solids with a tendency to crystallize but, provided the temperature is kept below the glass transition, the risk is pretty minimal in practice. How then can the same atoms be arranged in the condensed state in ordered or disordered ways? With all that similarity in the local environment of atoms, what geometrical rules can lead to periodicity in crystals and aperiodicity in glasses but in either case without any broken bonds?

Zachariasen was the first to conceptualize this for network glasses using ball-and-stick models arranged in rings of different sizes; later Bernal did so for metal structures by draining a paint can filled with ball bearings to find the points of contact. The arguments are illustrated in figures 6–8. You start with a pile of atoms like a pyramid of billiard balls. In two dimensions it is easier to see the consequences. The pile of atoms in figure 6 is arranged crystallographically in close-packed configuration, each atom surrounded by six others in regular arrangements. Two configurations are illustrated: each red is surrounded by four blues and two reds and each blue by four reds and two blues. This might represent a binary 50/50 alloy, although, even in the crystalline state, the arrangements could well be disordered with eight

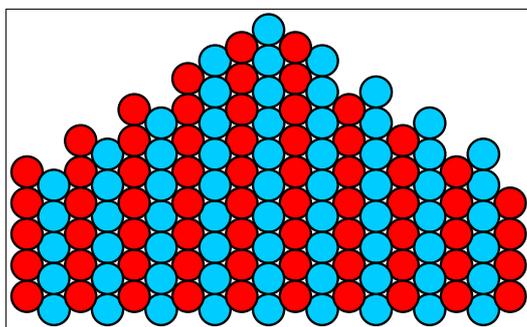


Figure 6. Pile of atoms.

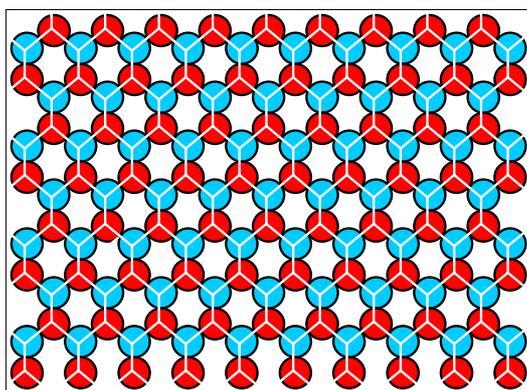


Figure 7. Crystalline network.

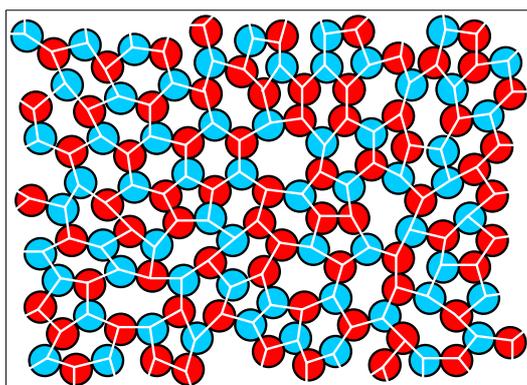


Figure 8. Continuous random network.

further configurations possible. The binomial expressions will tell you what the proportions are, but the take-home message is that the atomic configurations in a crystal are fixed and limited.

Networks structures like diamond or quartz, though, are not so tightly packed as metals like copper or gold, so we need to reduce the coordination number to generate realistic

structures. Figure 7 has been constructed from the same number of atoms but with the number of nearest neighbours reduced from six to three. Interatomic bonds have been drawn in and the angles between these are fixed. There is an obvious reduction in density compared with the metallic close-packed arrangement in figure 6. The triangular geometry in figure 7 is identical for each atomic site and there are two equivalent configurations of blues and reds. As with close-packed structures, crystalline geometries can support disorder—the extra configurations in this case totalling six. Figure 7 might model the structure of a III–V semiconductor like GaAs in two dimensions. If all the atoms were the same it would look like silicon or diamond.

Networks like the one shown in figure 7 are also characterized by rings, and the regular three-fold coordination here leads to identical rings of six atoms which, in the absence of disorder, comprise three reds and three blues. This is the point where the rules for disorder come in. Structural disorder can be modelled by introducing rings of different size. To do this and still retain the three-fold coordination, bond angles have to vary. This is illustrated in figure 8 and results in rings with five, six, seven or eight members. Because the local arrangements are tied to the interatomic potential (figure 5), the interatomic distance,  $r_0$ , is the same as before (figure 7), as is the coordination number of three, but now all possible nearest neighbour configurations of reds and blues occur. So this is the structure with the highest configurational entropy and internal energy<sup>1</sup>. It is also the least dense. There are fewer atoms in figure 8 than in figure 6 or 7. Configurational entropy forces density down. Most glasses are at least 10% less dense than their crystalline counterparts. Once the liquid state is reached all atoms are on the move and so the variety of local configurations becomes even more prolific than in the static structure of a glass. Different coordination numbers are possible and this is tied to a commensurate lowering of density. When alumina melts, for instance, the coordination number of aluminium falls from 6 to 4, and the density drops by 20%.

<sup>1</sup> If you want to generate three-dimensional structures with pupils, tetrahedral ball-and-stick kits can be instructive. Teams can be tasked with creating either a crystalline or a glass structure. Bear in mind that the glass structure is easiest to do. With crystals you need to keep ring sizes and rotation angles fixed.

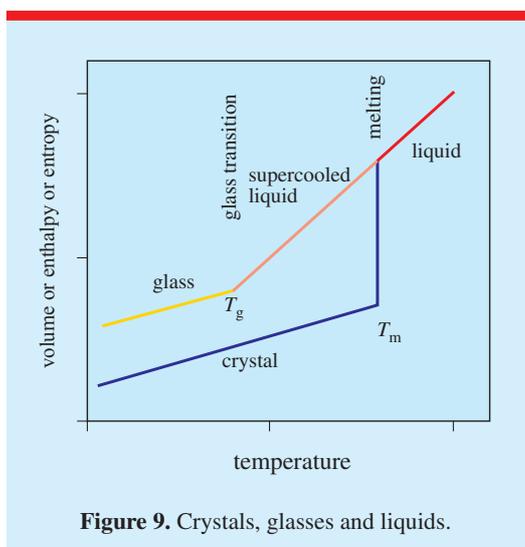


Figure 9. Crystals, glasses and liquids.

All this background about ordered and disordered structures enhances understanding of what happens thermodynamically at the glass transition or indeed when crystals melt. In figure 9 both of these processes are charted as the temperature rises or falls. Both atomic volume and entropy as well as enthalpy behave in similar ways. Concentrating on atomic volume, which is more intuitive, this is greater for the glass than the crystal (because of the larger number of configurations) but it also increases for both solids in virtually the same way—the thermal expansion following the asymmetric interatomic potential common to each (figure 5). When the crystal melts the atomic configurations shoot up, Dulong and Petit's law swings in and of course the atomic volume goes through a step function. What is less well known is that liquids expand faster than solids. This is because increasing configurational freedom demands more space. Fans need to leave the pitch before a game can start in order for the players to have room to operate.

Working in the opposite direction, when liquids are quenched, if the rate is too great for configurations to shake down and for crystallization to occur, the liquid becomes supercooled, the same thermal contraction extending from the liquid state, as figure 9 shows. Supercooled liquids are an area of huge research interest, with many weird and wonderful predictions—including temporary spatial and dynamic heterogeneity. In general though, as cooling continues, the viscosity escalates and eventually the supercooled state

converts to the glassy state, once the structural relaxation time exceeds the processing time.

*It will not have escaped the reader that these toy models of crystalline and glass structures each with different densities also offer scope for understanding symmetry, fractal geometries, space-filling methods, percolation etc. It also doesn't have to be atoms, it can be boxes of apples, soccer players on the pitch, agents in computer games, viruses spreading in epidemics and so on.*

## Summary

This picture of glass physics has been deliberately painted with a very broad brush, partly to cover the waterfront in one go, but also to demonstrate the rich variety of concepts and principles that can be taught subliminally if attention is focused on a fascinating material with a fabulous history. Traditionally we teach physics, certainly in higher education, as a hierarchical subject, excusing the abstruseness of fundamentals as the necessary discipline to understand the richness of the physical world. Curiosity, though, drives in the opposite direction, with the short attention span needed to keep disparate information in mind. This is how present society learns with its finger on the remote control button. The educational challenge, as always, is how to balance the old with the new. A subsequent article will look very much at the new—the way glass has entered information technology for example—and how it might find application in medicine.

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# A brief history of ... semiconductors

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## Abstract

The development of studies in semiconductor materials is traced from its beginnings with Michael Faraday in 1833 to the production of the first silicon transistor in 1954, which heralded the age of silicon electronics and microelectronics. Prior to the advent of band theory, work was patchy and driven by needs of technology. However, the arrival of this successful quantum theory of solids, together with a concentration on the growth of pure silicon and germanium and an understanding of their properties, saw an explosion in activity in semiconductor studies that has continued to this day.

## Introduction

One shouldn't work on semiconductors,  
that is a filthy mess; who knows if they  
really exist?

*Wolfgang Pauli, 1931*

Imagine a world without silicon. For physicists of my generation, educated in the late 1960s, this is just about possible. Thermionic valves had just about disappeared from the scene, and undergraduates were grappling with the discrete transistor. Not too much later came the integrated circuit or 'chip', and the rest is history. The ubiquity of the PC today and many other electronic devices (sometimes containing chips made out of materials other than silicon, but still, in the popular imagination, containing silicon chips!) means that people under about 30 probably could not exist without silicon.

Silicon belongs to a class of materials known as semiconductors, which also includes germanium (Ge), gallium arsenide (GaAs) and indium phosphide (InP). This class of solid is the essential element in all electronic devices today. Of these, silicon is by far the dominant material.

In this article, I am going to attempt to understand how the science and technology of semiconductors has developed into our present day situation. As a prelude, let us look at what is understood by a semiconductor.

The standard textbook approach is to say that a semiconductor has an electrical conductivity that lies somewhere between that of metals and insulators. For pure materials, figure 1 shows typical conductivities for metals, semiconductors and insulators. Semiconductors can be seen lying between metals and insulators; one important difference is that semiconductor conductivities are shown varying over several orders of magnitude. This is a very important property of semiconductors. We can vary the conductivity of semiconductors by doping the semiconductor, in a controlled fashion, with minute amounts of impurity atoms. Another important property of semiconductors is that this conductivity increases as the temperature of the material increases, whereas it will decrease in metals with increasing temperature. We can also increase the conductivity of semiconductors by shining light on them—a phenomenon known

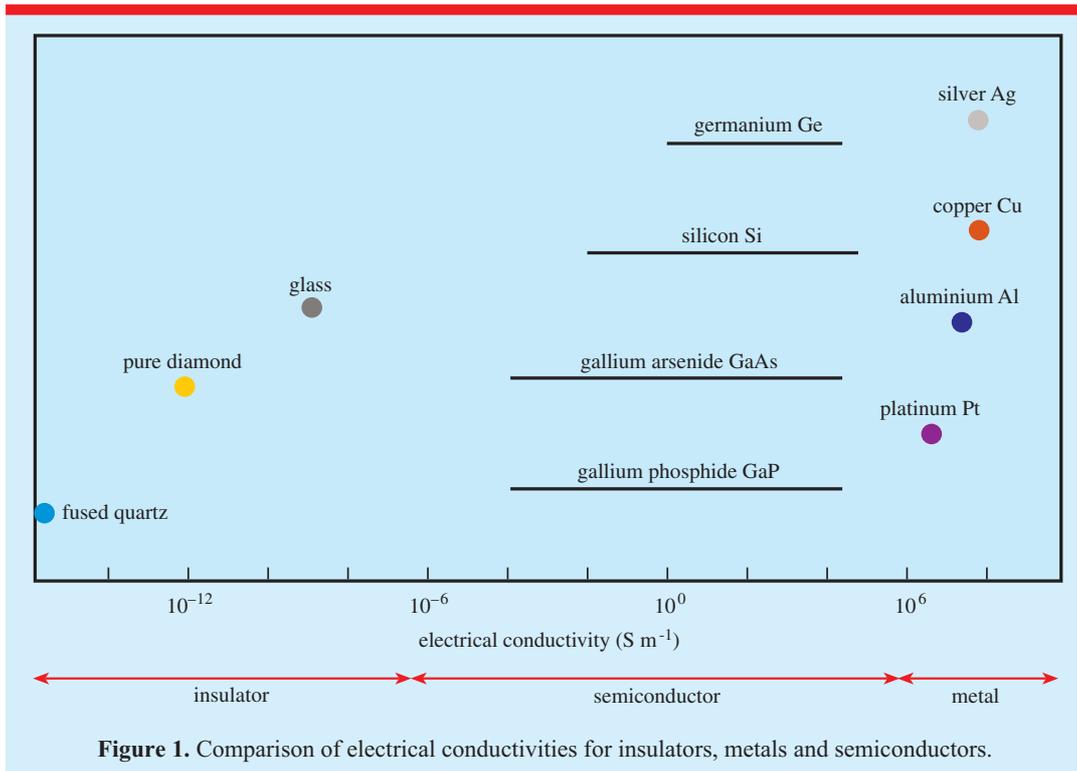


Figure 1. Comparison of electrical conductivities for insulators, metals and semiconductors.

as photoconductivity. We now understand these phenomena in terms of the quantum mechanics of electrons in solids, particularly the band theory of solids as developed by Wilson in 1931 [1]). This theoretical model represents one of the earliest and greatest triumphs of quantum mechanics.

### A nineteenth century phenomenon?

So, how far back should we go to understand the roots of semiconductors? Back to 1947 and the invention of the transistor or the 1920s and the formulation of quantum mechanics? We certainly cannot understand how semiconductors work without quantum mechanics. The first use of the word ‘semiconductor’ (or *halbleiter* in the German of the paper it was used in) to describe this class of material occurred in 1911 [2]. It might be a surprise to learn that semiconductor studies go back to the early nineteenth century. The pace of such work was slow during this time, partly due to a lack of engineering applications. Once these were found, the pace increased rapidly. Furthermore, the peculiar properties of semiconductors could not really be understood in terms of nineteenth century science (their properties were referred

to as ‘anomalous’ during this time), further explaining why semiconductors did not attract the attention of many scientists.

The discovery and investigation of electrical conduction in solids goes back as far as the eighteenth century, with the work of people like Gray (1731), Desagullier (1742) and Volta (1782). Humphrey Davey found that the electrical conductivity of metals decreases with increasing temperature. The earliest study of semiconductors is that of Michael Faraday in 1833. He investigated the temperature dependence of the electrical conductivity of silver sulphide (which he called sulphurette of silver). Such is the importance of this work to the development of semiconductors that it deserves to be described in Faraday’s own words [3].

The effect of heat in increasing the conducting power of many substances, especially for electricity of high tension, is well known. I have lately met with an extraordinary case, for electricity of low tension, or that of the voltaic pile, and which is in direct contrast with the influence of heat upon metallic bodies, as

observed and described by Sir Humphrey Davey.

The substance presenting this effect is sulphurette of silver. . . .

When a piece of this sulphurette, half an inch in thickness, was put between surfaces of platina, terminating the poles of a voltaic battery of twenty pairs of four inch plates, a galvanometer being also included in the circuit, the needle was slightly deflected, indicating a feeble conducting power. On pressing the platina poles and sulphurette together with the fingers, the conducting power increased as the whole became warm. On applying a lamp with the sulphurette between the poles, the conducting power rose rapidly with the heat. . . . On removing the lamp and allowing the heat to fall, the effects were reversed. . . .

Occasionally, when the contact of the sulphurette with the platina poles was good, the battery freshly charged, and the commencing temperature not too low, the mere current of electricity from the battery was sufficient to raise the temperature of the sulphurette; and then, without any application of extraneous heat, it went on increasing conjointly in temperature and conducting power, until the cooling influence of the air limited the effects.

Occasionally, also, the effects would sink of themselves and could not be renewed until a fresh surface of the sulphurette had been applied to the positive pole. . . .

Here we have a description of the increase in electrical conductivity with increasing temperature, a signature of semiconductor behaviour. We now know that this is due to the exponential increase in the number of charge carriers with temperature that dominates the decrease in the mobility of the carriers due to increased scattering by vibrations of the atoms. In metals, the number of carriers is essentially constant, so the electrical conductivity decreases with increasing temperature.

Of course, it could be (and it was argued for some time) that this was ionic conductivity. However, it was not until 1933 that it was

verified that this conduction in silver sulphide was electronic and not ionic [4]. (It is a little unfortunate that Faraday chose silver sulphide because its properties depend sensitively on the method of production of the material. It also undergoes a phase transition at 170 °C from an orthorhombic  $\beta$ -phase to a cubic  $\alpha$ -phase. Busch [5] gives a detailed account of the problems of this semiconductor, but this should not detract from the fact that this is the first, albeit qualitative, experimental observation of semiconducting behaviour.) It should be noted that Faraday has also observed thermal runaway in semiconductors as well as the problem of contacts and surface states!

The next date of note is 1839. At this time, a 19-year-old Alexandre-Edmond Becquerel, the father of Antoine-Henri, was experimenting with electrolytes. He worked with silver chloride-coated platinum electrodes in an aqueous nitric acid electrolyte. He noted that, if one of the electrodes was illuminated with sunlight, the emf generated between the electrodes increased [6]. This was the first reported instance of the photovoltaic effect, albeit not in a solid. The photovoltage was generated at the Ag/AgCl metal-semiconductor interface.

### **Semiconductor devices in the nineteenth century**

We now move forward to the 1870s. This was a crucial period in the progress of semiconductor science and technology. During this decade, two discoveries were made in the science of semiconductors that led to the development of the first semiconductor devices, significantly increasing the pace of semiconductor development.

In 1873, Willoughby Smith discovered the photoconductivity of selenium whilst working on submarine cables [7]. In his own words:

Being desirous of obtaining a more suitable high resistance for use at the Shore Station in connection with my system of testing and signalling during the submersion of long submarine cables, I was induced to experiment with bars of selenium, a known metal (sic!) of very high resistance. . . .

The early experiments did not place the selenium in a very favourable light for the purpose required, for although the resistance was all that could be desired... yet there was a great discrepancy in the tests, and seldom did different operators obtain the same results. While investigating the cause of such great differences in the resistance of the bars, it was found that the resistance altered materially according to the intensity of light to which it had been subjected.

The change in conductivity due to the absorption of light—photoconductivity—had been discovered although Smith considered selenium to be a metal. It would be another 14 years before Hertz discovered photoconductivity in metals! It was not until 1907 that selenium was shown conclusively to be a semiconductor. Although the effect was not used at this time, it led to one of the two major strands of semiconductor device engineering after this period, the photovoltaic cell. In 1876, William Grylls Adams and Richard Evans Day discovered that selenium produced electricity when light was shone on it [8].

The question at once presented itself as to whether it would be possible to start a current in the selenium merely by the action of light. Accordingly, the same piece of selenium was connected directly with the galvanometer. While unexposed, there was no action whatever. On exposing the [selenium] to the light of a candle, there was at once a strong deflection of the galvanometer needle. On screening off the light, the deflection came back at once to zero...

Light, as we know... tends to promote crystallization, and, when it falls on the surface of such a stick as selenium, probably tends to promote crystallization in the exterior layers, and therefore to produce a flow of energy from within outwards, which... appears... to produce an electric current.

The amount of electricity produced was very small and not enough to power anything, but at least it showed that solids could convert light into

electricity without heat or any moving parts! In addition to this effect, the paper indicates that they observed rectification (of which more below). Little note was made of this.

What is considered by many to be the first true photovoltaic cell was constructed by Charles Fritts soon after in 1883 [9]. The devices produced were still inefficient, transforming less than 1% of the absorbed light into electrical energy. This figure, however, was not to be improved significantly for many years. Fritts melted selenium into a thin sheet on a metal substrate and then pressed a very thin gold leaf film on the top surface as a second contact. This film was thin enough to allow light to penetrate to the selenium. The surface area of the film was about 30 cm<sup>2</sup> and the thickness around 30 μm. In passing, Fritts also observed rectification in his device.

In 1874 occurred the discovery of another effect that was to have a profound influence on the development of semiconductor devices. This was the discovery of rectification in the contacts between metals and some oxides and sulphides. The most systematic study of this phenomenon was by Carl Ferdinand Braun, who studied the flow of electric current between various sulphides such as galena (lead sulphide) and thin metal wires touching the sulphides—the so-called ‘cat’s whiskers’. Braun had made the first semiconductor rectifier, the foundation for the most basic and simple electronic device, the diode. Indeed, it has been argued that Braun’s discovery heralded the era of electronic devices in the twentieth century. (Initially, Braun worked with silver wires with the ends flattened and pressed hard onto the galena. In 1883, he discovered that the rectification was enhanced when one of the metal contacts was sharpened to a point.)

With a large quantity of natural and artificial metallic sulphides and greatly varying pieces, the most perfectly formed crystals that I could find as well as coarse samples, I discovered their resistance varied with the direction, intensity and duration of the current. The differences amount up to 30% of the total amount [10].

In the same year, Schuster observed rectification in the contact between tarnished and untarnished copper wire. The copper oxide on the tarnished wire acted as the semiconductor.

These rectifiers saw little practical use until the experiments of Hertz in 1887, showing the existence of radio waves. Initially, a device known as the coherer was used to detect these radio waves but it was found to be difficult to use and insensitive. Braun himself had begun to experiment with wireless telegraphy in 1898 and, in 1901, used semiconductor rectifiers for the reception of wireless signals. Also active at this time was Sir J C Bose, who took out the first patent for a semiconductor rectifier made from galena [11]. The patent was filed in 1901. The scene was ready for a significant leap forward in semiconductor technology, with the emergence of both silicon and germanium as semiconductors of note.

### And so to the twentieth century

With the increasing use of radio, and the development of semiconductor rectifiers (even though the mechanism of rectification was a mystery), the prospects for semiconductors must have seemed bright at the beginning of the twentieth century. Of special note at this point is Greenleaf Whittier Pickard, who worked for AT&T between 1902 and 1906. During this period, he worked on wireless telephony using semiconductor rectifiers. Pickard tested a large number of materials in order to discover the most effective detector of radio waves. It is said that he tested in the region of 30 000 materials, of which some 250 proved to be effective as rectifiers. Of particular note, Pickard used fused silicon that he obtained from the Westinghouse Electric Company and found this material to be the most stable of the rectifiers he tested. In 1906, Pickard filed a patent on a silicon crystal detector for radio waves [12]. Thus, silicon made its entry onto the semiconductor stage.

The patent application indicated that Pickard thought the rectifying effect to be of thermal origin, as was widely believed at the time. However, even in 1878, Braun had concluded that rectification was neither an electrolytic nor a thermoelectric process, but he believed that the behaviour was similar to the behaviour of a gas discharge. It was not until 1938 that Braun's hypothesis was confirmed by Schottky [13].

It was not too much longer before germanium appeared on the scene as well. In 1915, Carl Benedicks published a paper on 'Electric

properties of rare metals' [14]. Benedicks was a Swedish scientist, well known for his work on metals. In this work he used germanium, which had been presented to Uppsala University by its discoverer, Clemens Winkler. He noted that the resistance of his germanium lay between that of silicon and tin, and also produced a rectifier in the material using point contacts of platinum and copper. The two major players in the next phase of semiconductor development had now arrived on the scene.

These rectifiers or 'cat's whisker' diodes had their limitations. They required careful adjustment and could easily be knocked out of alignment. In addition, at around this time, vacuum electron tubes (thermionic valves) were being developed (see [en.wikipedia.org/wiki/Vacuum\\_tube](http://en.wikipedia.org/wiki/Vacuum_tube) for a brief history of thermionic valves and their development). Sir John Ambrose Fleming had developed a diode in 1904 [15] based on a thermionic valve that acted as an efficient detector of radio waves (he called his device an oscillation valve). In 1907, Lee de Forest took out a patent for a three-electrode thermionic valve (a triode), in which an additional electrode (grid) was placed between the anode and cathode in the diode valve. He called this device an Audion [16]. It was soon recognized that, by applying a small voltage to the grid, the flow of relatively large currents though the valve could be controlled. The grid allowed the triode to operate as a power amplifier for an analogue signal. With valves producing significant amounts of power, it was possible to transmit speech and music—the broadcasting industry was born. Interest in the semiconductor diode detector waned rapidly.

### The birth of the transistor

Nature abhors the vacuum tube.

*J R Pierce, Bell Labs engineer who  
coined the term 'transistor'*

Interest in semiconductors began to revive in the 1920s with the development of barrier layer rectifiers and photovoltaic cells, in particular devices made from copper oxide and selenium. The former were made by growing cuprous oxide on a plate of copper whilst, for the latter, selenium was melted and spread on to a metal washer. The rectifying interface was a relatively large area, unlike the cat's whisker devices, and it could

handle larger currents. These devices went into commercial production, finding uses in battery chargers, exposure meters in photography, in modulators and nonlinear circuit elements.

During this period, engineers were becoming interested in communications at higher and higher frequencies. In particular, the development of radar was crucial. At these sorts of frequencies (the first practical radar operated at around 300 MHz and the magnetron worked at 3 GHz in 1940), valves were unreliable and noisy due to interelectrode capacitances. However, point contact semiconductor diodes had very low internal capacitances and so were seen as ideal for this application.

The 1930s saw a renaissance in semiconductor development, chiefly due to the pressures of impending war and the need to develop radar. In addition, the band theory of solids, which has become fundamental for an understanding of the behaviour of semiconductors, arrived with the seminal work of Alan Wilson in 1931 [1]—quantum theory meets semiconductors! In this theory, the electron states in a crystal exist as bands of energy separated from each other by energy gaps, in which, in a pure crystal, there are no allowed energy states. This picture was able to explain the difference between insulators, metals and semiconductors based on the idea of filled and empty bands. In addition, it also showed how the controlled introduction of small amounts of particular impurity atoms into a semiconductor could strongly influence the electrical conductivity. Band theory immediately explained the exponential increase of electrical conductivity with increasing temperature, and the existence of bipolar conduction in semiconductors (electrons and holes). The scene was now set for the explosion of experimental and theoretical work in the field of semiconductors.

The earliest work in this period was in the UK using point contact diodes made of silicon. This silicon was about 98% pure, with the main impurity being aluminium (but crucially also boron and phosphorus, which are difficult to remove from silicon). Unfortunately, these cat's whisker diodes tended to behave erratically on occasions, and in the early stages of radar it was common for an operator to carry a number of these diodes and search for one that worked, replacing it if it stopped working or behaved erratically.

This behaviour was believed to be due to the impure nature of the silicon that was used. This sparked a push to produce pure silicon, an event that should be seen as a transformation in the fortunes of semiconductor theory and devices. A metallurgist, R S Ohl, initiated the effort in 1935 at the Bell Laboratories. The best material was obtained by sealing the highest purity silicon available in a quartz vessel, heating it up past its melting point and then allowing it to cool slowly. As the melt cools and freezes from the top surface, there is a segregation of impurities. Depending on the type of impurity, impurities are redistributed through the silicon. By cutting a relevant section out of the ingot, a highly pure piece of polycrystalline silicon could be obtained. In this way, 99.999% pure silicon was available by 1942. It was noticed that, when a piece of silicon was cut from one of the ingots, rectification was observed [17]. In addition, the diode thus produced showed a very strong photovoltaic effect, the first time this had been observed in silicon. By good fortune, p-type impurities (boron) and n-type impurities (phosphorus) had redistributed themselves during solidification of the silicon, with a sharp boundary between the two regions. The silicon had been cut perpendicular to and including the interface boundary, producing a p–n junction diode rectifier—serendipity indeed! This controllable way of forming a junction would give more reliable diodes than the point contact, cat's whisker diodes.

Work on producing p–n junction diodes in germanium began again at about this time. In 1942, work was underway at Purdue University under Karl Lark-Horowitz, originally on lead sulphide but rapidly moving to studying germanium and the production of high purity germanium [18]. Germanium belongs to the same group in the Periodic Table as silicon, but melts at a lower temperature (937 °C compared with 1415 °C for Si) and is not as reactive as molten silicon. This made it a very attractive proposition, and soon high quality germanium cat's whisker diodes were being used in radar circuitry as a result of the high purity germanium being produced. These diodes had excellent rectifying properties and high current-carrying capacity. The work was not only technological but produced an enormous amount of knowledge about the physics of semiconductors. It was this

improved understanding and the availability of high quality germanium that led to the production of the first transistor.

During this period of development of the diode, a number of scientists had thought about producing the solid-state equivalent of the triode valve, which could be used as an amplifier. (A poll amongst Bell Lab staff for a name for this semiconductor triode can be found at [www.bellsystemmemorial.com/pdf/transistorname.pdf](http://www.bellsystemmemorial.com/pdf/transistorname.pdf). The eventual name was, of course, the transistor, short for *transfer varistor*.) The most frequently proposed solution was based on the field effect, whereby an electric field, applied through the surface of a semiconductor, would modify the density of mobile charge carriers (electrons or holes) in the bulk of the solid and hence its electrical conductivity. The earliest proposal for such a transistor device goes back to 1925 [19], and William Shockley, a seminal figure in the development of the transistor, was reported to be trying to make a field effect transistor in 1940.

The end of the war saw a change in emphasis of semiconductor work, with emphasis now on economic benefits of semiconductor technology. A team was brought together in Bell Laboratories in 1946, including Shockley, John Bardeen and William Brattain, with the intention of improving the understanding of semiconductors and the development of devices that might replace the short-lived and high-power-consuming thermionic valves currently being used in automatic telephone dialling and switching and microwave radios. An important decision made at the inception of this work was to concentrate only on silicon and germanium as material for possible devices.

The initial work to produce a field effect transistor failed. Theory indicated that this was because the electric field did not penetrate the bulk of the semiconductor but was terminated by charge carriers trapped in quantum states associated with the surface. Bardeen and Brattain set out to confirm this hypothesis, attempting to control and modify the surface states. Using germanium with metal point contacts on the surface, they surrounded the metal contacts with electrolytes. An evaporated gold spot adjacent to the contact later replaced the electrolyte. (Gold forms an ohmic, **not** a rectifying, contact to Ge.) Finally, the contacts were replaced with two strips of gold foil, separated by about  $50\ \mu\text{m}$ , pressed onto the

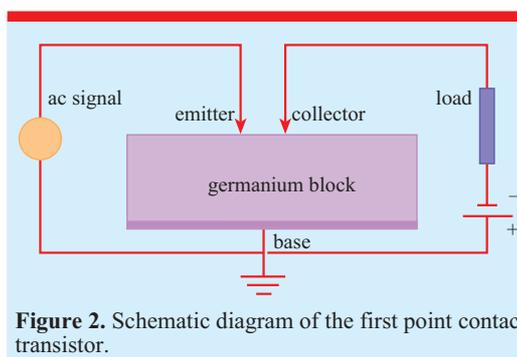


Figure 2. Schematic diagram of the first point contact transistor.

germanium surface. To achieve this, a single strip of gold foil was attached over the point of a plastic triangle. With a razor blade, the gold was sliced through at the top of the triangle. The whole triangle was then held over a crystal of germanium using a spring, so that the contacts lightly touched the surface. The germanium sat on a metal plate attached to a voltage source. With one gold contact forward biased and the other reverse biased, power gain was observed and the transistor effect had been discovered [20]. This event took place on 16 December 1947. On 24 December, positive feedback was applied to the device and oscillation occurred—the acid test of power gain. For the next few months, frenzied work was performed to understand the operation of the device, to determine applications and to sort out patenting. The momentous discovery was announced in June 1948, by which time the gold foil had been replaced by two closely spaced point contacts about  $50\ \mu\text{m}$  apart (figure 2). The point contact transistor had arrived. Bardeen and Brattain received the Nobel Prize for this discovery, together with Shockley, in 1956 (figure 3).

There was controversy as to the mechanism of this transistor. Was it a surface effect (as believed by Bardeen and Brattain) or a bulk effect? Shockley believed it was a bulk effect and concluded his analysis with a proposal for a different type of transistor—the junction transistor [21]. This was a sandwich of a thin, lightly doped piece of n-type semiconductor between two regions of p-type semiconductor. If one p–n junction was forward biased and the other reverse biased, this would produce power gain. This was the junction transistor.

In February 1948, John Shive applied two phosphor bronze contacts on opposite sides of a



**Figure 3.** Left to right: Shockley, Bardeen and Brattain. Photograph reprinted with permission of Lucent Technologies Inc./Bell Labs.

100  $\mu\text{m}$  thick piece of germanium and transistor action was observed. The length of the surface around the semiconductor, from contact to contact, ruled out a surface effect. Transistor action had been proved to be effectively a bulk effect as described by the theories of Shockley [22].

Because the point contact transistor was difficult to make, difficult to control and unstable, effort was now made to produce a junction transistor. Initial efforts used polycrystalline semiconductor material, but the use of such material, where charge carriers would be scattered and trapped unpredictably by grain boundaries and twins, would produce devices that were irreproducible and of low quality, hardly a good thing for mass production. It was recognized, notably by Gordon Teal, that what was needed was high purity, single crystal material.

The use of single crystal materials for semiconductor devices was controversial at this time. Much of the progress in this field was due to a team led by Teal. In 1948, Teal and John Little grew a single crystal of germanium based on a technique developed by Jan Czochralski in 1918 [23]. Teal used a small single crystal (known as a seed crystal) taken from a large

polycrystalline rod of germanium. This was dipped in a melt of germanium, rotated and slowly withdrawn, or pulled, from the melt. As the seed crystal is withdrawn from the melt, the molten germanium adhering to the crystal solidifies, using the crystal structure of the seed as a template. In this way, large single crystals of germanium were grown, which could be doped in a precise fashion [24]. In April 1950, Teal's team grew a single crystal of germanium containing a thin region of p-type material embedded in an n-type material. As the seed crystal was pulled out of an n-type germanium melt, gallium was quickly added to make the melt p-type. When a layer of p-type material had formed of the required thickness, antimony was added to the melt. This compensated the gallium and turned the melt back into n-type material. This crystal was cut into n-p-n rods and contacts applied to the three regions of doping [25]. The electrical properties of the transistor thus made were largely consistent with Shockley's proposed junction transistor. This transistor was more reliable than the point contact version, generated less noise and could handle higher powers. The junction transistor was now the rival of the thermionic valve ... if only it could

be mass-produced. The problem was that only one region or slice of, say, p-type material could be grown in one crystal to produce an n–p–n transistor (and vice versa for a p–n–p transistor). This was a very expensive way to make devices. In 1952, John E Saby at the General Electric Company came up with the solution by producing the alloy transistor [26]. This germanium alloy transistor was the first to be readily manufactured.

The pieces of the jigsaw are now almost all in place. The final piece was to make transistors from silicon. From the outset, it had been recognized that silicon would make a superior transistor to germanium. Silicon has a larger bandgap than germanium. The number of electrons and holes generated by thermal energy in pure silicon is much less than in pure germanium. These thermally generated carriers lead to reverse currents in a p–n junction, which can degrade device performance. The problem was to grow single crystals of silicon, which, in its melt state, is very reactive with any container. Following the growth of single crystal silicon in 1952 [27], H C Theurer, using a ‘floating zone’ technique [28], produced single crystals of silicon with a purity commensurate with that of the best germanium (one impurity atom in  $10^{10}$  silicon atoms!). The starting silicon material did not need support in a vessel and hence the contamination problem was effectively removed. In this way, silicon crystals with a purity level of the best germanium were produced. In 1954, Teal announced the first silicon transistor at a meeting of the Institute of Radio Engineers in Ohio. The rest, as they say, is history.

### Conclusion

Just as the electrical conductivity of semiconductors shows an exponential increase with temperature, so activity in semiconductors shows an exponential increase with time (even to the present day!). The real take-off point occurs with the understanding of the theory of semiconductors and the almost simultaneous production and experimental investigation of highly pure germanium and silicon. However, it may be truly said that semiconductors were discovered in the nineteenth century. All the fundamental properties of semiconductors had been observed during that century.

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# Fantastic plastic

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## Abstract

Various properties of polymers can be demonstrated using these simple tricks and recipes that were previously described in the 2002/3 IOP Schools and Colleges Lecture.

In 2002/3 the UK Institute of Physics Schools and Colleges Lecture was entitled *Fantastic Plastic*. Although a one-hour talk about plastic doesn't sound too exciting on the face of it, *Fantastic Plastic* seemed to strike a chord, and schools are still asking for it for their Year 10 students (age 14–15).

Fortunately the Engineering and Physical Sciences Research Council (EPSRC), who funded the development of *Fantastic Plastic*, is continuing to provide funding for the talk to visit UK schools. UK schools who are interested in booking it and are less than two hours from Southampton should e-mail Averil Macdonald on a.m.macdonald@reading.ac.uk.

Also, the University of Surrey, where the talk was originally developed, has now provided funding for a *Fantastic Plastic* Teaching Resource CD, through its Widening Participation initiative. This resource, which will be mailed out to all UK schools, will contain copies of the images from the talk, transcripts of the facts and anecdotes, short videos of the demonstrations, and directions for how to produce the various materials to do the demonstrations yourself. It is expected to arrive in schools in December 2005.

However, if you can't wait for it, here are some of the tricks and recipes to try for yourself.

## Disappearing water

This is a quick demonstration to show that plastics often have unexpected properties with applications in everyday life—in this case, disposable nappies.

## Required:

- Sodium polyacrylate (may also be known as poly(acrylic acid), sodium salt)
- Vending cup
- Water

## Method:

- Put a teaspoon of sodium polyacrylate into the bottom of a vending cup.
- Pour in a few millilitres of water, wait a few seconds.
- Turn the cup upside down (over the head of a favourite student?).
- Nothing will come out as the water will have been locked into the polymer.

## Explanation

Sodium polyacrylate is a polymer, consisting of chains of identical repeat units:



There is a relatively strong interaction between the electronegative  $\text{COO}^-$  groups on the polymer and polar water molecules. When the sodium polyacrylate is immersed in water, the sodium ions dissociate from the polymer and are dispersed in the water. Several water molecules replace the charge lost by the displacement of each sodium ion and are loosely held in place. Hydrogen bonding between neighbouring molecules holds additional water within the polyacrylate gel.

Dry sodium polyacrylate is a white powder. It will absorb over 500 times its mass of water, creating a gel that is dry to the touch. For this reason it is used in the manufacture of disposable nappies and other absorbant products.

*How does a nappy work?*

Cutting open the lining of a disposable nappy and teasing apart the fibres will show up the crystals of sodium polyacrylate. The amount of sodium polyacrylate determines the absorbancy of the nappy. Pouring large amounts of water into a range of nappies can be used as a test of their absorbancy and thus the amount of sodium polyacrylate used in their manufacture. A more complex investigation might associate the cost of a nappy with performance.

*Reappearing water*

Required:

- Salt
- Water-soaked sodium polyacrylate

Method:

Put water-soaked sodium polyacrylate into a petri dish. Add salt (generous amount). Water will seep out. The salt destroys the gel, releasing the water.

*Discussion opportunity*

Parents in the UK currently throw away around eight million disposable nappies every day and they take around 200 years to degrade. In the meantime they are taking up huge amounts of space in landfill sites. A discussion of the pros and cons of disposable and fabric nappies will include consideration of the environmental impact of the huge cost of landfill compared with the impact of generating the electricity, producing the washing powder and dealing with the waste water required for washing fabric nappies. Interestingly, Australia is so worried about the problem that it has launched a disposable nappy recycling scheme where the nappies are separated into the components for reuse. An alternative would be biodegradable nappies, but although a biodegradable nappy is possible, the manufacturers have undertaken market research that indicates that the consumer would not be prepared to pay the extra cost.

**Cutting a liquid (or the self-syphoning gel)**

This is a useful demonstration that polymers are made of long chain molecules. Contrast the behaviour of this viscoelastic polymer liquid with a more typical liquid composed of small, individual molecules that can easily move past each other.

The solution should be made up in advance and can be kept for many months in a sealed container. *It is not recommended that students make up the solution themselves—or that they try cutting the liquid. This is best done as a demonstration by the teacher.*

Required:

- 25 ml water-soluble anhydrous alcohol (such as ethanol or isopropyl alcohol)
- 3–4 g poly(ethylene oxide) (high molecular weight)
- stirring rods
- two 600 ml beakers
- colouring, e.g. food colouring or fluorescein (optional but fun!)
- scissors

*Note.* Do not substitute poly(ethylene glycol) for poly(ethylene oxide) as the former is the lower molecular weight substance as used in antifreeze.

Method:

- Mix 25 ml alcohol with 3–4 g poly(ethylene oxide) in a clean dry beaker.
- Add 350–400 ml tap water in one pour and stir until the polymer powder has dissolved. As you stir, the viscosity of the polymer solution will increase.
- Add colouring if required.
- Pour liquid from the first beaker into the second beaker and cut with scissors. The liquid will ‘snap’ and spring back into the first beaker when it is cut.

*Note.* Only try to cut the liquid with the upper beaker held almost upright and not leaning over because gravity will make it continue to pour and make a real mess of your scissors (see figure 1). This takes practice!

This polymer is extremely slippery and great care should be taken when handling beakers if they have the liquid on the outside as a result of a less than professional attempt at the experiment!



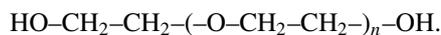
**Figure 1.** Take care when cutting the liquid.

#### *Alternative demonstration*

When pouring, raise the upper beaker and the gel will often syphon back into it. This takes practice, is not always easy to see and works best with a solution of particularly high concentration.

#### *Explanation*

Polymers are long chain molecules made up by joining together the same molecular groups (or repeat units) to make a long chain. The repeat unit for poly(ethylene oxide) is shown below. In this scheme,  $n$  represents the number of times the unit is repeated, typically several thousand.



Notice that every third atom along the chain is an oxygen atom. This oxygen readily forms hydrogen bonds with water, giving the polymer a very high solubility in water.

Long polymer molecules intertwine or 'entangle' with each other, just like spaghetti on a plate. These physical entanglements allow polymer solutions to bear some mechanical stress. The molecules are usually coiled up, but when stress is imposed on them they can straighten out somewhat. When the stress is released, they coil up again. This coiling process gives the polymer its elasticity. When the solution is cut and the stress

is suddenly released, this elasticity is dramatically demonstrated.

Whereas all polymers in solution will have physical entanglements that lead to viscoelastic behaviour, there is an additional factor at work in poly(ethylene oxide). Water molecules can bridge two adjacent polymer molecules by forming hydrogen bonds. These bridges create a strong network of molecules. A three-dimensional network of molecules in a solution is referred to as a gel.

The gel, once made, can be kept for many months in a watertight container.

#### **Making slime**

This a fun class activity to demonstrate that the properties of a polymer can be changed by crosslinking the long chains so that they are 'tied' together. Such materials are often used for special effects in films.

#### *First make PVA solution*

This should be made up in advance and given out to pupils after it has cooled.

Required to make 1 litre of solution:

- 25 g polyvinyl alcohol (98–99% hydrolysed, with a molecular weight between 100 000 and 200 000)
- glass beaker
- heater/stirrer
- thermometer

Method:

- Put 25 g PVA into a dish and add cold water until it is covered.
- Allow to stand for at least 20 minutes.
- Preheat 1 l water in a beaker to between 70 °C and 90 °C.
- Drain excess cold water from the PVA.
- Start the stirrer and add PVA to hot water in small amounts—this stops it from clumping.
- Keep stirring until all the PVA has dissolved.
- Allow solution to cool before use.

*Note.* PVA may form a gel clump at the bottom and has to be broken up if this happens.



Figure 2. Slime always appeals to students.

*To make slime from PVA solution*

This is a simple class activity that can be used from age 10–18.

Required by each group:

- A few ml cold PVA solution (prepared as above)
- Saturated sodium tetraborate solution (Borax)
- Small beaker
- Stirring rod
- Pipette

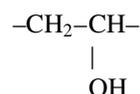
Method:

- Place PVA solution in the beaker (add food dye if preferred).
- Add a few drops of sodium tetraborate solution and stir; keep adding until the required consistency is achieved. Typically a ratio of 12 : 1 by volume gives a good result (figure 2).

Slime will keep well if in a sealed plastic bag but can easily leak out if not properly sealed. Students can handle slime but must wash their hands afterwards and must not feed it to anyone else!

*Explanation*

Polyvinyl alcohol (PVA) consists of long chains with this repeat unit:



The sodium tetraborate solution creates bonds, or crosslinks, between the long chain PVA molecules at random positions. When crosslinking is complete, all of the millions and millions of PVA molecules are joined together to form a single, huge molecule consisting of an extended three-dimensional network. The slime can be considered to be a chemically crosslinked gel. The number of crosslinks per unit volume (or per molecule) determines the final consistency of the slime. A very runny slime has fewer crosslinks than does a more solid variety.

Whereas the self-siphoning poly(ethylene oxide) slime (see above) consisted of physical entanglements and relatively weak hydrogen-bonded crosslinks, the PVA contains stronger chemical crosslinks.

*Note.* Soluble laundry bags are also made of polyvinyl alcohol. As well as demonstrating to students that some plastic bags dissolve in water (always a surprise), they can be used as an alternative way of making the PVA solution required for making slime. In this case dissolve one bag in 500 ml warm (not boiling) water. The recipe for slime is the same. Soluble laundry bags are widely used in hospitals and can be bought from many outlets online for around £8.00 for 25 bags. The big advantage of such soluble laundry bags is that they reduce the contact between health workers and contaminated linen and thus reduce the chance of infection.

**Making potty putty**

This is a fun class activity demonstrating how crosslinking changes the properties of the polymer.

Required:

- PVA glue (polyvinyl acetate), e.g. from school stores
- Saturated sodium tetraborate solution (Borax)
- Stirring rod

**Method:**

- Add one teaspoon of PVA glue to a small-diameter container.
- Add a few drops of sodium tetraborate solution.
- Stir and keep stirring. The trick is to use as little sodium tetraborate as possible because this gives a more pliable potty putty. This will take a long time (~15 minutes).
- If too much Borax solution is added the polymer will crosslink very quickly and the result will not be very pliable and may be quite friable. This a typical result from students with insufficient patience.

When the putty is dry to the touch (no longer sticky), it can be removed and kneaded by hand. The crosslinking process is slow, so the more you knead the better. Potty putty will keep well in a sealed plastic bag.

*Note.* Honey spoons provide a clean way to hand out small quantities of PVA glue.

*Explanation*

This is yet another example of linking together molecules via chemical crosslinks. In this case, the polymers are not dissolved in water or other solvent. The putty is not a gel, but simply a crosslinked polymer network or ‘rubber’. The bonds between the polymers add to its stiffness. The elasticity of the putty results from the coiling and uncoiling of molecules, just as in the self-siphoning gel (see above).

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## Plastics—COSHH (hazard) assessment

### Sodium polyacrylate

#### *Procedural hazards*

Hazard from inhalation of dry powder.

#### *Health hazard*

Can be absorbed, by inhalation.

May cause mild irritation of upper respiratory tract.

Dust may cause reddening/drying of affected area with possible burning or other discomfort.

#### *First aid*

Eyes: flush with water of approved eye wash and obtain medical aid if irritation persists.

Inhalation: remove from source; seek medical aid if discomfort continues.

### Poly(ethylene oxide)

#### *Procedural hazards*

Hazard from inhalation of dust and eye contact with particulates.

No hazard from skin contact.

#### *Health hazard*

Eyes: dust may cause discomfort of eye with slight redness and possible swelling of conjunctiva.

Inhalation: dust may cause irritation of respiratory tract experienced as nasal discomfort and discharge.

Ingestion: slightly toxic; may cause abdominal discomfort, nausea and vomiting.

#### *First aid*

Eyes: immediately flush eyes with water and continue washing for several minutes. Obtain medical attention.

Skin: wash with soap and water.

### Poly(vinyl alcohol)

#### *Procedural hazard*

Making solution: only hazard is from scalds from the hot water.

#### *Health hazard*

PVA may be harmful if absorbed through skin. May cause eye irritation.

May be harmful if inhaled—irritant to mucous membranes.

#### *First aid*

Skin contact: wash with soap and water.

Eyes: flush with running water for at least 15 minutes.

Ingestion: wash out mouth if conscious; seek medical aid.

### Sodium tetraborate

#### *Procedural hazards*

Hazard from skin contact on damaged or broken skin.

#### *Health hazard*

Can be absorbed across skin, by inhalation or by ingestion.

Acute effects of exposure:

Eyes: dust may cause mechanical irritation.

Skin: may cause irritation.

Ingestion: may cause headaches, excitement, fatigue, nausea, vomiting or coma. May cause kidney damage.

Inhalation: respiratory tract irritation, chronic effects as for ingestion.

#### *First aid*

Ingestion: if conscious give 2–4 cups milk/water to drink. Seek immediate medical aid.

Inhalation: remove from source; seek medical aid if breathing difficulties appear.

Eyes: wash with water; seek medical attention if irritation persists.

#### *Personal protection*

Goggles and gloves to be worn for solution preparation of sodium tetraborate.

#### *Storage and disposal*

Store in cool dry place.

Dry waste disposed of through normal waste route.

Liquids may be flushed away as a dilute solution.

# Tomorrow's plastic world

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## Abstract

Far from being just cheap packaging materials, plastics may be the materials of tomorrow. Plastic can conduct electricity, and this opens up a host of high-tech possibilities in the home and in energy generation. These possibilities are discussed here along with how plastic can be recycled and perhaps even grown.

Metals are conductors of electricity. Plastics are insulators. Wrong!

For years we have been teaching that plastics do not conduct electricity. After all, plastic is used as insulation around the copper wires in ordinary electrical cables. Yet as long ago as the 1970s Alan J Heeger, Alan G MacDiarmid and Hideki Shirakawa made the revolutionary discovery that plastic can be made electrically conducting. For this they were awarded 2000 Nobel Prize in Chemistry.

Plastics are polymers, molecules that repeat their structure regularly in long chains. For a polymer to be electrically conductive it must 'imitate' a metal—the electrons must be freely mobile and not bound to the atoms. One way of achieving this is for the polymer to consist of alternate single and double bonds, termed conjugated double bonds, between carbon atoms. It must also be 'doped', which means that electrons are removed (through oxidation) or introduced (through reduction). These 'holes' or extra electrons can move along the molecule so the polymer becomes electrically conductive.

## The story of conducting polymers

The story begins in the 1970s. Shirakawa was studying the polymerization of acetylene (a black powder). A researcher accidentally added one thousand times more catalyst than usual—and a silvery film formed on the surface of the liquid

in the vessel. The obvious question was: 'If the plastic looks like a metal, can it conduct electricity like a metal too?'

The silvery film was not a conductor, but a few more modifications led to a reaction of the polymer film with iodine vapour. This oxidation reaction caused electrons to be removed and the conductivity increased by ten million times. This was what led to the award of the Nobel Prize.

Polyacetylene is, unfortunately, no good for practical use as its conductivity drops rapidly in contact with air. This has led to the development of more stable, conjugated polymers, e.g. polypyrrole, polyaniline and polythiophene. Now we are able to produce ordinary transistors, field effect transistors, photodiodes and light-emitting diodes in plastic. By combining the mouldability and low weight of plastics with the conductivity of metals we can look forward to a wide range of commercial developments.

For the full story see [nobelprize.org/chemistry/educational/poster/2000/index.html](http://nobelprize.org/chemistry/educational/poster/2000/index.html)

For a detailed explanation of the science behind this see [nobelprize.org/chemistry/laureates/2000/chemadv.pdf](http://nobelprize.org/chemistry/laureates/2000/chemadv.pdf)

## What does this mean for us?

Flat screen televisions have been available for a while. These 'plasma screens' are based upon

small light-emitting tubes (like mini fluorescent tubes) directly behind the screen that emit light to form the image. It is well known that these screens are less bright than conventional televisions, cannot be viewed from oblique angles and do not last very long. Perhaps they are not such a good investment.

The next generation of flat screen televisions will be based upon electroluminescent conducting plastics—semiconductive plastics that glow when a voltage is applied to them. This effect was first reported in 1990. Different formulations give rise to the emission of different colours. These screens will be only 3 mm thick and will be lightweight and flexible. We can look forward to televisions we can roll up for storage and carry round before hanging on the wall. And, of course, there will be no need to locate the television near to the DVD player or set-top box and connect them using Scart leads because the various devices will communicate by microwaves. The same electroluminescent plastics technology will be applied to the displays of mobile phones and it will be possible to watch videos on your wristwatch.

See [www.cdtltd.co.uk/technology/36.asp](http://www.cdtltd.co.uk/technology/36.asp)

### Other life changes promised by conducting polymers

On a larger scale, smart windows will be made of plastic that alters its light transmission characteristics when a voltage is applied. This will do away with the need for curtains and blinds at windows. It will also be possible to arrange for the window to reflect heat into the room in winter but away from the room in summer.

The process that produces electroluminescence can also be 'run backwards'. Absorption of light creates positive and negative charges that are picked up by the electrodes, providing an electric current. This is the principle of the solar cell. Solar cell plastic could be spread out over large areas to provide environmentally friendly electricity. Polymers will also be incorporated into rechargeable batteries to eliminate the need to use polluting heavy metals.

An electronic 'nose' already exists in which the conducting properties of the polymer are affected by the volatile materials, and this has applications in areas from perfumery to the detection of illicit substances—anything that

currently requires a sniffer dog. And the sense of taste has not been forgotten. Polymers that change their electrochemical properties when sweet or salty substances stick to them are being developed—though the applications are less certain.

For more detail on these applications see [www.memagazine.org/backissues/april98/features/plastics/plastics.html](http://www.memagazine.org/backissues/april98/features/plastics/plastics.html)

Some polymers are being developed that can change their shape with the application of an electric field. This could pave the way for artificial muscles to power prosthetic limbs responding to the nerve impulses in the remaining tissue.

### Plastics on our food

In fact plastic electronic circuits will be printed onto items using a technology related to ink-jet printing. Bar codes on packaging will be a thing of the past, as will the supermarket checkout. Instead the plastic electronic circuit on each of the items will be interrogated by a device as you pass through an archway which instantly totals your spend and debits your bank account. IBM is already developing these, so anyone planning to take a job on a supermarket checkout will need to think again!

These same circuits will be interrogated by the computer that has been integrated into your fridge. In fact designs exist for a fridge with a screen in the door so that it can be used either as an internet connection or as a television. In fact, if you choose to do your grocery shopping online the fridge computer can make up your list for you based upon the items it detects in itself and communicate it to the supermarket for delivery. The same computer will have the facility to search the web for recipes that use the ingredients you have to hand—taking into account your need to restrict your calorie or carbohydrate intake—and suggest what you might have for dinner tonight. The ability of the packaging on food to change colour as the food approaches its 'best before' date will alert you to the need to use things quickly or throw them away. The same technology will print plastic circuits onto the labels in clothing, allowing the washing machine to select the most appropriate wash cycle—so no more annoying 'colour runs'.

### Plastics helping the environment

The environment is also set to benefit from the impact of polymers. Hydrogen fuel cells will power the cars of the not so distant future with zero pollution and no need for politically sensitive oil supplies. The hydrogen fuel cell works because of a polymer called Nafion. This acts as a solid electrolyte or proton exchange membrane sandwiched between the anode and cathode. Hydrogen is fed to one side and oxygen (from the air) to the other. The protons from the hydrogen are transported through the polymer but the electrons cannot pass through. Instead they pass through wires connecting the two sides, powering any device in the external circuit on the way. This is similar to the action of a battery except that the two chemicals required are constantly fed to the membrane and so the fuel cell does not go flat. When the reconstituted hydrogen and oxygen meet they form water, which is the only waste product of the process. For those worried about vast quantities of water lying in the road it is worth pointing out that the quantity of water produced is minimal and will evaporate quickly. The supply of hydrogen may be through electrolysis of water, possibly powered by solar or wind energy. The hydrogen is then likely to be stored in cylinders made of metal hydrides or even carbon nanofibres, though research is still on-going on that point. Anyone uncertain about the likelihood of this happening should realize that Los Angeles has already restricted access to the city centre to zero-pollution cars and that hydrogen filling stations are already open in California, Las Vegas, Munich and Reykjavik, Iceland! These filling stations are being run by consortia of oil companies. If the oil companies didn't think it was the way forward they wouldn't invest their money.

For more details on fuel cells see [science.howstuffworks.com/fuel-cell3.htm](http://science.howstuffworks.com/fuel-cell3.htm)

For a fuel cell kit with over 30 experiments based upon the various components see [www.heliocentris.com/products/genius.html](http://www.heliocentris.com/products/genius.html)

### Plastic in the Third World

If that all sounds far too focused on self-indulgent consumerism it's worth noting that plastics are coming to the aid of the world's most needy. Victims of natural disasters need readily

constructed shelters. A form of polystyrene (the same polymer used for drinks cups) has been developed with sufficient robustness to build houses. Not only are they affordable but they are also energy efficient (polystyrene has long been used to keep hot things hot and cool things cool) and earthquake resistant! The idea is to cover the basic polystyrene shell with chicken wire and then a thin layer of concrete.

For the story of the polystyrene homes see [news.bbc.co.uk/1/hi/technology/3528716.stm](http://news.bbc.co.uk/1/hi/technology/3528716.stm)

### How to recycle plastic

Of course, plastics are typically derived from oil products and it is well known that our oil reserves are dwindling fast. There's already pressure on us to recycle plastic products, but separating all those different polymers is time-consuming and, at present, not financially attractive. However, with legislation in the pipeline to ensure that higher proportions of plastic items are recyclable, companies such as Ford are putting large amounts of money into research that will enable polymers to be separated as easily as magnets distinguish between aluminium and steel cans in a scrap metal yard. Research at the University of Southampton is pointing to the idea of using tribology to distinguish between polymers (see figure 1). This relies on friction between two materials generating an electric charge (think rubbing balloons on jumpers). Whether the charge generated on the polymer is positive or negative depends upon what it was rubbed against, and this can be used to



**Figure 1.** The Tribopen is a simple hand-held plastics identification tool.

distinguish polymers from each other ready for recycling.

More information can be found at [www.soton.ac.uk/~wolfson/applications/apps-plasidentandrecycle.shtml](http://www.soton.ac.uk/~wolfson/applications/apps-plasidentandrecycle.shtml)

### How to grow plastic

It would be better to find a means of producing polymers from more plentiful sources. And this is already possible. PHB (or polyhydroxybutyrate) is a plastic that is fully biodegradable. But better than that: by taking two genes from a bacterium that makes PHB and putting them into the chloroplasts of the leaf of a cress cell, the genetically modified cress cell produces PHB when it photosynthesizes, instead of the usual polymer, starch. The future may see plastic grown in fields.

More information can be found at [www.firstscience.com/site/articles/sykes.asp](http://www.firstscience.com/site/articles/sykes.asp)

### The plastic age

To conclude, plastic may seem a very straightforward material for very low-tech applications, such

as plastic packaging and toys. In fact this couldn't be further from the truth. Within a generation there may be very few items relying on materials other than polymers. An interesting activity would be to go through and list items currently made from metal or ceramic or some other class of material, then work out what properties each item requires and whether, in fact, a polymer could do the job just as effectively. Maybe, just as we moved from the copper age to the bronze age to the iron age we are about to move from the present steel and heavy metal (i.e. uranium not rock) age into the polymer age.

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