

Transparent Conductors: Invisible Materials with High Technology Applications

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Abstract: *The use of visual display devices in digital wristwatches, electronic calculators, pocket televisions, laptop computers, and compact camcorders, is not possible without the development of special materials, such as “transparent conductors”, which are at the same time, transparent and good conductors of electricity. In this article, we describe briefly these materials and highlight their physics unusual properties.*

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1. Introduction

One might immediately associate the word CONDUCTOR to the metals such as copper (Cu), silver (Ag), and gold (Au). Apart from being good electrical conductors, metals have their “*metallic luster*”. Metals are so shiny because they reflect most of the visible light that reach them. However, not only the metals, other materials such as silicon (Si), germanium (Ge), and gallium arsenide (GaAs) are also good reflectors of light, provided their surfaces have mirror finished polishing. The last three materials are semiconductors, optically opaque, but have metallic luster. The main objective of this article is to define conductors that, at the same time, are transparent, which is contrary to our general knowledge on a metal. Though the topic appears to be a bit confusing, as we will see, it is just the matter of understanding the physics behind. To understand that physics, first we need to understand a few basic things about materials.

Atoms and the Formation of Solid

We all know that the matter is made of minuscule particles called “*atoms*”. Until the end of the 19th century, atoms were believed to be indivisible particles, little hard spheres, just like marbles. Nevertheless, at the beginning of the 20th century, it was demonstrated that atoms are composed of even smaller particles. The atom was then modeled as a miniature of solar system. In the planetary model of the atom, *electrons*, the negatively charged particles, behave as planets, orbiting the atomic *nucleus* consisting *protons* and *neutrons*. While a *proton* has same amount of charge as that of electron, it is positively charged. On the other hand, a *neutron* is neither positive nor negative (neutral). An atom in its most stable state has no net electric charge because the net positive charge of protons is balanced by the negative charge of electrons of equal number. The planetary model for an isolated atom assumes rotation of the electrons around

the nucleus, with well defined circular trajectories (figure 1), called “*orbitals*” [¹]. In the case of gases, one can imagine that atoms or molecules (chemically bonded groups of two or more atoms) move freely in the available space, except for occasional collisions between them (figure 2a). In this case, electronic orbitals can still be considered to be circular.

In the case of liquids, atoms or molecules are not as free as in gases, though they might have a net average motion along a particular direction (figure 2b). Finally, in the case of solids, the movement of particles is much more restricted. In a solid, each atom is anchored to a fixed position and it can only vibrate around that place (figure 2c). An atom in a solid is under the influence of its surrounding atoms through strong cohesive force. The collective interaction of atoms in a solid manifests as a change in electron trajectories (these trajectories are responsible for the apparent size of the atom). As the atoms in a solid are very close to each other, their electronic orbitals mix - up to form so called “*bands*” consisting of closely spaces electronic levels [²].

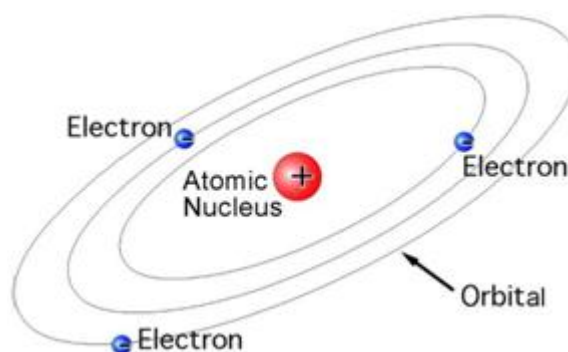


Figure 1: Planetary model of atomic structure

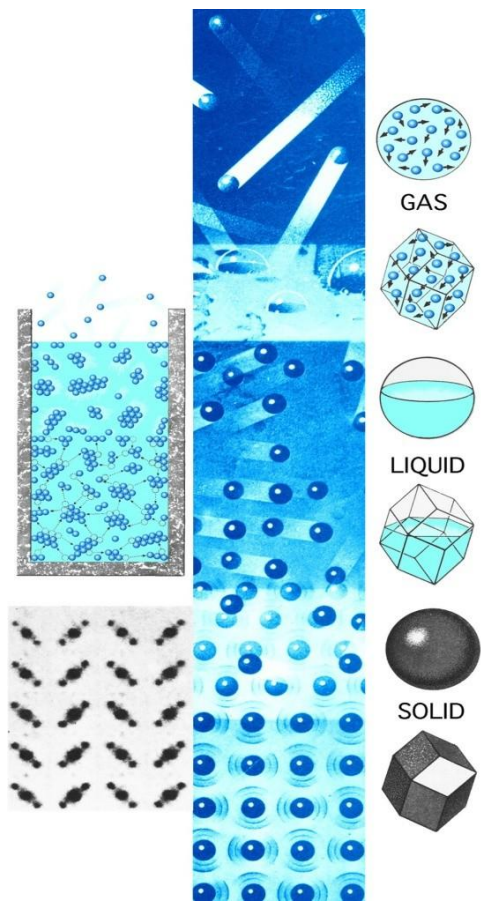


Figure 2: Three physical states of matter: a) gaseous, b) liquid, and c) solid.

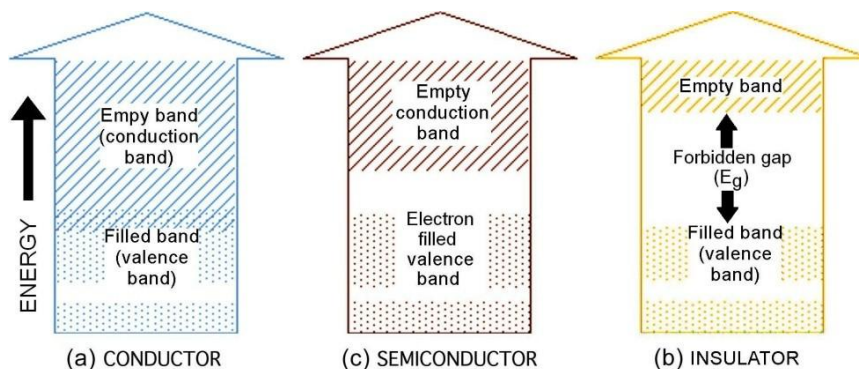


Figure 3: Electronic band schemes for: a) metal, b) insulator, and c) semiconductor.

In order to “take a longer ride”, an electron needs to be freed from its original place; *i. e.* it must move to a place (energy level) that allows more movement. That place is the next higher energy level which is completely empty. Once there, the electron is free to move throughout the whole material.

The movement of electrons in a particular direction inside a material is known as *electric current*, and that is why this outer band is known as the *conduction band* (figure 3).

To go from valence band to the conduction band, an electron must “jump” over the gap that separates them. The energy gap between the valence and conduction bands is known as the *forbidden gap* and normally no electron can be found there.

Electronic Band Model of Solids

In the planetary model of atoms, there is no restriction to the number of possible orbital’s for the electrons (planets); thus the number of electronic levels can be infinite too. Nonetheless, neither all the electronic orbitals, nor all the energy levels are fully occupied by electrons, due to the finite number of electrons in each atom. The available electrons progressively fill the energy levels. The first one to be occupied is that closest to the nucleus, *i. e.* having lowest energy. If we continue placing the electrons in higher energy levels (farther away from the nucleus), there will be one “last” occupied energy level in the outermost part of the atom; which certainly not the last allowed energy level, but by then we would be out of electrons. These electron - filled or fully occupied energy levels form the so called *valence band* (figure 3) of the solid as the electrons in this band are the ones that determine the chemical behavior of the atoms, which are shared or transferred between the atoms in the process of formation of molecules through *chemical bonding*. Valence electrons (electrons at the valence band) cannot go far away from the nucleus to which they are associated. They can only “go to visit the next - door neighbor”, staying there or returning to its original atom depending on the nature of bonding.

Electrical Properties of Solids

The band model of solid allows us to classify materials as conductors, insulators, and semiconductors. In a conductor there is no such thing as a forbidden gap. The energy gap is nonexistent, and the valence and conduction bands are *overlapped* (figure 3a). Thus, there are always available electrons for conduction. The outermost electrons can move through the solid with minimum external force, as the slightest “breeze” drags the dust in its way.

In an insulator, the width of the forbidden gap is so big that at room temperature (~ 300K), it's really hard for the electrons to attain enough energy for jumping to the conduction band (figure 3b). So they don't conduct electrical current at room temperature.

Conductors and insulators are two extreme cases, either

there is no energy gap or it is huge. However, there are intermediate cases known as *semiconductors* (being halfway between opposite cases; they can also be called as *semi-insulators*). In semiconductors, there exists an energy gap between the bands but of “reasonable” dimension (figure 3c). Even at room temperature, there would be a small number of electrons in the conduction band of semiconductors, which allows them to conduct electricity; of course, not as fluent as conductors.

We have seen that both conductors and semiconductors are able to conduct electricity. There is, however, a way for distinguishing these two types of material. In conductors, if it is not too cold, there are always a plenty of electrons available for conduction due to the superposition of valence and conduction bands. An increase in temperature would increase the energy of conduction electrons leaving its number almost unchanged. The vibrations of the atomic nuclei that make up the solid would also increase. An increase in these vibrations increases the rate of collision between the atoms and their free electrons, which make it more difficult for the electrons to move in a specific direction (electric current). The difficulty to establish an electric current in a material, faced by conduction electrons, is known as electrical *resistivity*. The resistivity of conductors *increases* along with temperature due to higher collision rate at higher temperature. In the case of

semiconductors, the increase of temperature notoriously increases the number of available electrons in the conduction band. In comparison to the increase in free electrons in the conduction band, the increase in atomic vibrations is almost negligible in a semiconductor. Thus, the *resistivity* of a semiconductor decreases as the temperature increases.

The Nature of Light

In the second half of the 17th century, the eminent English physicist Sir Isaac Newton speculated that bodies produce light by sending beams of luminous particles, called *corpuscles* of light. However, according to the Dutch physicist Christiaan Huygens, bodies emit light by pulsing and giving origin to waves in the environment that surrounds them; similar to the ones produced by a stone when it hits a pond (figure 4). Since then, the physics of optics has been evolved, and the theories of optical phenomena are created. Finally, in 1893 the Scottish physicist and mathematician James Clerk Maxwell proposed a theory considering the close association among light, electricity and magnetism, which at the present time is known as the *electromagnetic theory*. The theory is based on classical and undulatory concepts. This classical model of the radiant energy holds that such energy is produced every time an electric charge oscillates or it is accelerated.

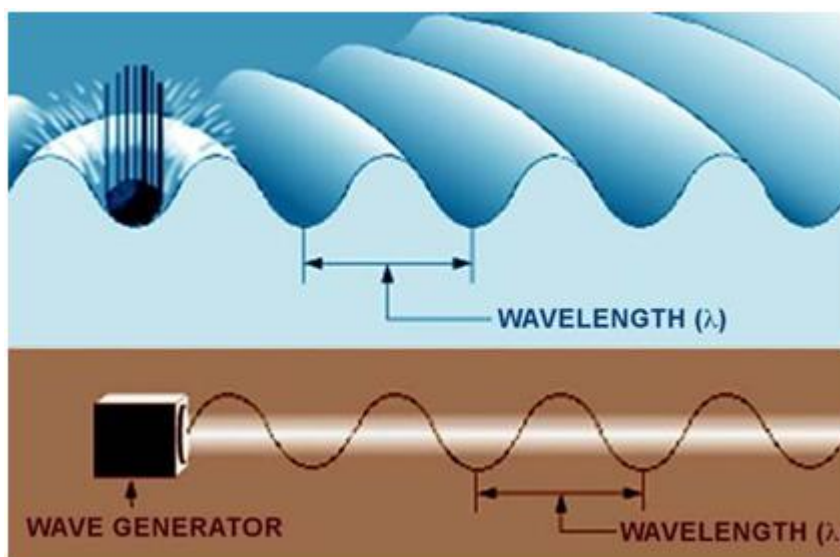


Figure 4: Generation and propagation of an acoustic wave

The apparent movement of this charge is a perturbation characterized by the presence of electric and magnetic waves traveling together. This is why this perturbation is called *electromagnetic wave*. Let us look a bit deeper into this model for visible light and for all electromagnetic radiations.

Undulatory theory presents electromagnetic radiation as a continuous wave generated by a vibrating system, similar to the waves generated at the water surface on throwing a stone (figure 4). Two important properties of a moving wave are its speed and the wavelength. It has been proved experimentally that the speed c , of every electromagnetic radiation is the same, 300,000 km/s in vacuum. Wavelength is represented by λ , and is defined as the distance in between two successive crest or two successive valleys of

the wave (figure 4). While the wavelength of water waves can reach several centimeters or meters, visible radiation has a very short wavelength. For example, the light that appears violet to our eyes has a wavelength of approximately 0.4 μm or 400 nm. Red light has a wavelength of approximately 0.7 μm or 700 nm (μm , “micrometer” = millionth of a meter, and nm, “nanometer” = millionth of a millimeter).

Now, if we were in free space and could count the number of electromagnetic waves with different wavelength that cross a particular point every second, we would see that the waves would be traveling at the same speed c , and there will be more number of waves when there λ is shorter. The number of waves that crosses a specific point per second is called *frequency* of the electromagnetic radiation and is

represented by n . So, if the wavelength is shorter the frequency of the electromagnetic radiation will be higher, as they are related each other by the equation: $c = n\lambda$.

However, at the beginning of 20th century, the German physicist Max Planck suggested that a matter does not emit radiation in a continuous way, as classical physics proposed, but it does in a discontinuous way but in little packets, which he called “*quanta*”, a Latin word that means quantity. The energy of a quantum increases while the frequency of the emitted radiation increases. Though the Planck’s theory was not well received among the scientific community as it was against the well established principles of physics, Albert Einstein took the Planck’s theory to solve the problem known as the *photoelectric effect*. This effect consists in the emission of electrons by some materials when they are illuminated. In fact, the radiation can pose both particle and wave character. Considering Planck’s idea, Neils Bohr, a Danish physicist proposed the planetary model of atom that

we have talked about earlier.

Optical Properties of Solid

As has been discussed earlier, solid materials are characterized by their energy bands. The band filled with electrons is known as valence band, and the next external band, generally unfilled, is called conduction band. To make an electron of the valence band to jump to the conduction band, we need to supply some energy. The minimum energy necessary to happen that is equivalent to *forbidden gap* of the solid. This energy can be supplied in the form of heat or light.

Now, if the frequency of the incident radiation is such that the energy of its “*quanta*” is equal or higher than the value of the forbidden gap, this radiation will be absorbed by the electrons of the valence band, prompting them to jump to the conduction band (figure 5).

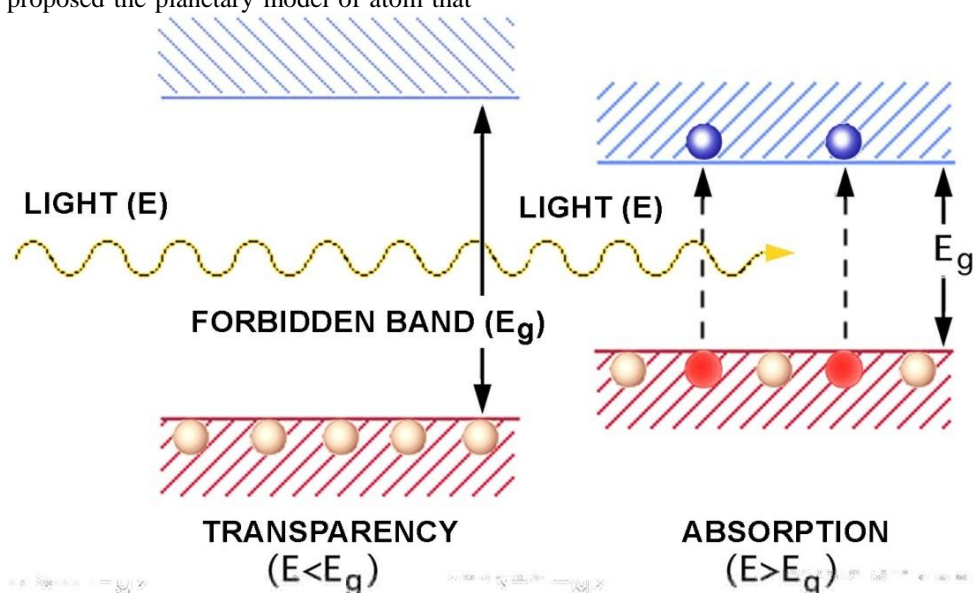


Figure 5: Energy band diagram of a semiconductor and its interaction with radiation (light)

When the frequency of the incident/illuminating radiation is below this value, the energy of its “*quanta*” won’t be enough to make the electrons reach the conduction band, and the “*quanta*” won’t be absorbed by the solid. This radiation will pass through the material without disturbing the electrons of the valence band, *i. e.* the solid is transparent to this radiation (if the frequency of the incident radiation diminishes too much, it can also be absorbed by the solid, but in the form of heat). Optical behavior of solid depends basically on the way the radiation interacts with the material.

Therefore, we can infer that a solid will be transparent to a bigger range of frequencies if its forbidden gap is wider. Insulators are the material with a wider forbidden gap. This may explain why the glass and the quartz are excellent insulators and at the same time transparent to visible light. Of course a material does not need to be transparent to the visible light to be a good insulator; but the truth is that all the materials transparent to light have forbidden gaps wider enough to stop the electrons from jumping to their conduction bands either by absorption or heating.

So, we reach to an apparent “*impasse*”. Smaller the size of

the forbidden gap better would be the electrical conductivity of the solid material. But having good conduction implies the material will be less transparent to visible light. Then, how can we talk about transparent conductors?

Transparent Conductors: Better When Not “Pure”

The secret of the above question lies in a relatively simple fact. As you may remember, an atom in its natural state is *electrically neutral*. When the atoms are bonded together to form a solid, these characteristic will not be lost. But being in a solid, if an atom releases one or more of its electrons (under an external force like an electric field), though the solid as a whole would be electrically neutral, the distribution of electric charge between the constituting atoms would be unbalanced, and the atom in question gets *ionized*. In this case, as the total positive charge of the atom is greater than the total negative charge of its electrons, it turns out to be a *positive ion*. On the contrary if somehow the atom “*accepts*” one or more electrons than what it had in its natural state, then it gets negatively ionized.

Nevertheless, it must be noticed that, despite an atom in a solid gets ionized, the material remains electrically neutral

due to the fact that the material as a whole has not lost any electron. In a solid, it is more common that an atom releases some of its electrons and gets ionized positively. While the released electrons can move through the material easily, the positive ions left behind cannot. When an electron is released from an atom, the chemical bonding that we have been talking about in previous section will be incomplete. Due to the loss of electron(s), the positive charge of the atomic nucleus will not be balanced. From the concept of bond formation, we can consider the place from where the electron is released as a center of positive charge. This positive charge generated through the vacancy of an electron in the chemical bond or at the energy level is known as "hole" (figure 6).

The "hole" concept is very important in the study of materials, in particular of semiconductors. Even for a highly pure semiconductor, it is common to find a good number of "holes" in its valence band and as much free electrons in its conduction band.

Under an electric field, the electrons move to the positive pole and "holes" move in opposite way. In fact, the "holes" do not move; what happens is that an electron from a neighboring atom jumps on to fill the "hole" – the space left behind due to the release of an electron, which apparently gives the feeling that the "hole" is moving to the opposite direction to the electron.

Now what would happen if somehow we can replace an atom of a semiconductor by another having one more valence electron than the original one? On incorporating this new atom into the rigid solid structure, its extra electron would find no room in the neighboring atoms or bonds to be accommodated. Therefore, as an "abandoned child" this abandoned electron will join with the existing free electrons created by thermal excitation. Addition of more of such external atoms to the semiconductor will add up more free electrons in excess, and the number of "holes" will no longer balance the number of free electrons (figure 7).

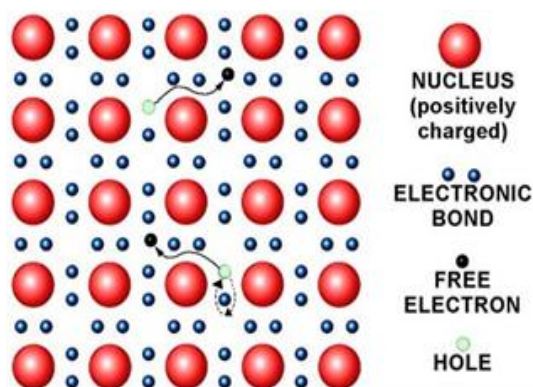


Figure 6: Creation of free "electrons" and "holes" in a solid

At this situation, as the total number of free electrons in the semiconductor is higher than the number of "holes", major part of the electric current produced on applying an electric field would be generated due to the participation of those free electrons, and the semiconductor would be called n -type (n for negative) semiconductor. The incorporated external atoms with higher number of valence electrons than the host atoms are known as n -type impurities or donors.

The opposite would happen if, instead of having one more valence electron with respect to that of the host material, the strange/external atom has one less electron. On incorporating such an atom into the host semiconductor, one of the links/bonds with the neighboring atoms would be incomplete. There would be a missing electron, and hence the creation of a "hole". Similar to the "free electrons" in n -type semiconductors, this "hole" would be free (not bonded), and their number will increase if more and more such external atoms are incorporated into the host semiconductor. When the number of these free "holes" are higher than the number of free electrons in the host semiconductor, there would be a charge imbalance (figure 7), and the semiconductor is called p -type (p for positive). Those external atoms having lesser valence electrons than the host atoms will create "holes" in excess in the valence band, and are known as p -type impurities or acceptors (acceptors of electrons) [3].

We must not think that these are the only ways to achieve excess carriers (electrons or "holes") in a semiconductor. Suppose, instead of incorporating external atoms into the semiconductor, we "kidnap" some of their own; so to say, we create some spaces inside the semiconductor where some atoms are missing. In physics we call these atom - missing spaces as "vacancies".

Now what would happen in terms of charged careers at these places? Well, there are two possibilities. The first possibility is the missing atoms may leave their valence electrons behind, without disturbing the charge balance of the neighbor links/bonds. The vacancy in this case can be treated as "neutral" vacancy (as it does not contribute excess electron or hole to the electrical conduction) (figure 8a). Obviously, as these left - behind electrons no longer have their "family" and are only "adjoined", it's easy to "persuade them" for leaving the place, swelling the lines of conduction electrons.

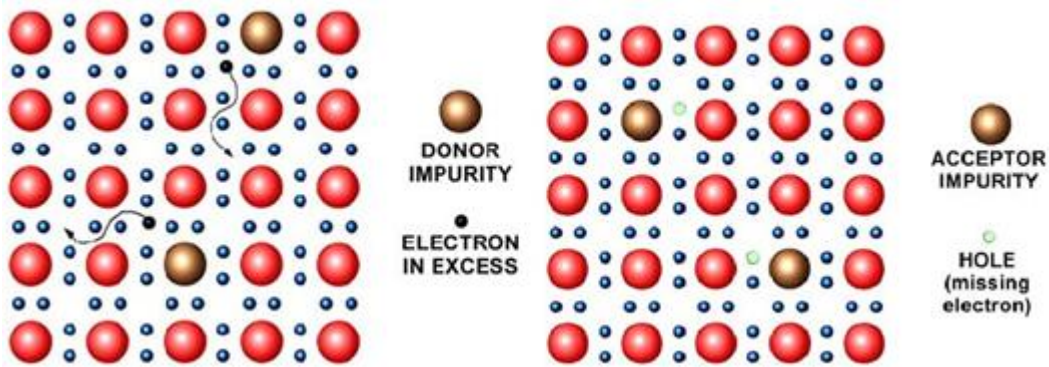


Figure 7: Donor and acceptor impurity atoms in n - and p -type semiconductors (left and right, respectively).

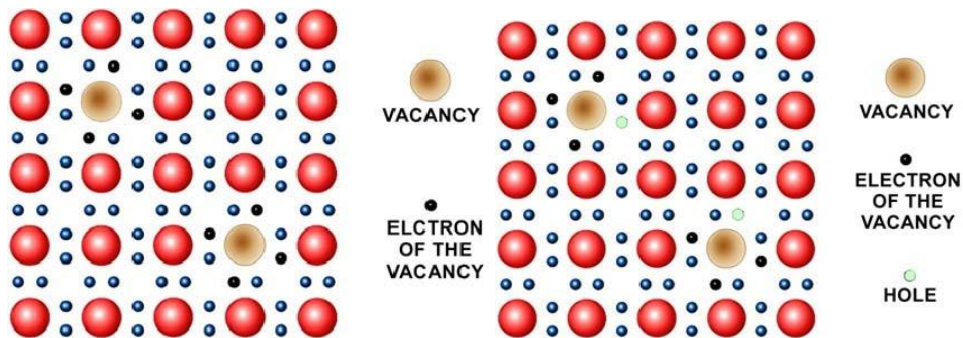


Figure 8: Creation of excess electrons and holes in a semiconductor through vacancy formation

The other possibility is when the missing atom takes away some or all of its valence electrons while leaving the solid host (semiconductor), leaving the neighboring links/bonds incomplete. This way the vacancy would generate some “holes” (figure 8b). So, the creation of vacancies can also alter the concentration of electrical charge carriers in the semiconductor. However, unlike the impurities, the vacancies are not necessarily donors or acceptors. Rather, the nature of the vacancies would be always “doubtful” (donor or acceptor). These vacancies are amphoteric in nature.

The introduction of impurity atoms or the creations of vacancies in a semiconductor produces some energy levels in the forbidden gap (figure 9).

In general, the new energy levels – set off by the introduction of impurities or the creation of vacancies - are very close to the conduction or the valence band (depending on the nature of the impurity atoms or the charge state of the vacancies). In the case of donor type impurity or negatively charged vacancies the generated energy level is called donor level, and as acceptor level for the opposite case. Again, if the number of introduced impurities is high, the corresponding energy level (in the forbidden gap of the semiconductor) can convert to a band, increasing its width with the increase of carrier concentration, even with the possibility of merging (or intermingling) with the nearest

valence or conduction band. Nevertheless, despite those possibilities, the width of the forbidden gap does not change drastically. Therefore, though the intentional introduction of impurities or creation of vacancies can modify drastically the electrical resistance of the semiconductor, its optical transparency to visible light remains almost unaffected. This is how we can obtain materials which are good electrical conductors (even though are not as good as metals) and at the same time, transparent to visible light. To conclude our discussion on the origin of optical transparency in transparent conductors, we need to talk a little more about the electrical and optical properties of solids [4]. As you may recall, when we established the differences between conductors, insulators and semiconductors, we talked about their electrical resistance. In the case of the conductor, we learnt that its electrical resistance increases with temperature, while in the case of semiconductor it happens to be opposite.

In fact, the electrical resistance is not the intrinsic characteristic of a material. Rather, it depends on its physical dimensions (length, width, and height) too. What is intrinsic to the material is a property called *resistivity*. This property does not depend whether the bit of material has greater or lesser dimensions (well, up to a certain limit). It depends on how easily the electrons can move inside a solid. The easiness with which the charge carries can move through materials is known as *mobility*.

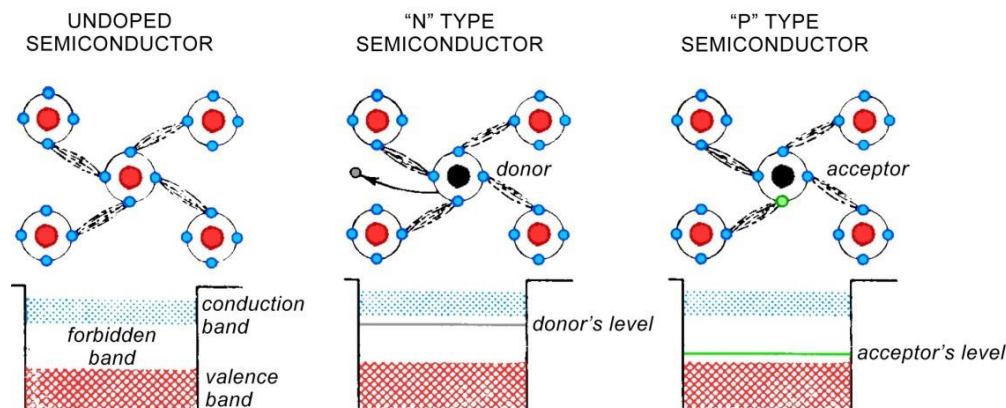


Figure 9: Atomic bonding in undoped and doped semiconductors and their energy band diagrams.

The term “*mobility*” is associated to the charge carriers of a material, not the material itself. As expected, such easiness depends –among other things - on how many carries in a unit volume of the material are. If the density of the charge carriers in a semiconductor (electrons or *holes*) is high, during their movement under an electric field they collide frequently, and hence can not move forward easily.

In a solid, frequently the atoms are well arranged with some specific regular pattern, and we call whole material as crystal. However, frequently a solid does not have all the constituting atoms well arranged (especially when they are in thin film form). The whole material may contain several regions with ordered atomic arrangements, but each region might have different atomic order. Such materials are called polycrystalline materials. In the latter case, the charge carriers in the solid apart from the normal resistive barrier face additional barriers at the zone in between these small crystal grains, called *grain boundary*. Both the charge carriers and the radiation travelling through such polycrystalline materials would encounter scattering at the grain boundaries, frequently changing their travel directions. In this case, we can talk only about the average kinetic behavior of the charge carries or the radiation [5].

Generally, the transparent conducting materials have high band gaps and high free carrier concentrations. Though these materials are generally semiconductor in nature, due to high band gap value, they are transparent to the visible light (energy in between 3.0 and 4.0 eV) and high free carrier concentrations make them highly conductive.

To end the present discussion, we must consider that the optical properties of a solid can be affected due to the change in direction of the incident light beam inside a solid while propagating through. The phenomenon is known as *refraction*, which is measured by an index, called *refractive index*. Greater the refractive index of the material, greater the light beam deviates from its original path while travelling through it. As the value of refractive index of a solid increases, its transparency to the visible light decreases. This particular characteristic of solid is very much important for practical applications of transparent conductors.

The most promising transparent conducting materials are some metal oxides. Due to this particular characteristic, they are called *transparent conducting oxides*. For most of the

technological applications, these transparent conducting oxides are used in “thin film” form. Transparent conductive layers of cadmium oxide (CdO) were first reported by Bädeker [6] whom prepared these thin films by thermal oxidation of sputtered metallic cadmium films. Though, very thin ($\sim 100 - 200 \text{ \AA}$) films of metals such as gold (Au), silver (Ag), and copper (Cu) have also good transparency and are good conductors, generally they are not very stable and their properties change with time. On the other hand, coatings based on semiconductor materials such as CdO and SnO (tin oxide) are more stable, and have superior hardness than the metallic thin films.

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Conflict of interest

The authors declare that there is no conflict of interest in the current article.

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