Review

Semiconductors

Semiconductors can be divided into two classes: elemental semiconductors, which contain only one type of atom, and compound semiconductors, which contain two or more elements. The elemental semiconductors all come from group 14.

Chemical Equilibrium in Solid

$$\mathrm{Si}_{\text{(crystal)}} \rightarrow h^+ + e^-$$

$$K = [h^+][e^-] = p \times n$$

$$[h^+] \approx 1.5 \times 10^{10}\ \mathrm{cm}^{-3}$$

Compound semiconductors maintain the same *average* valence electron count as elemental semiconductors—four per atom. For example, in gallium arsenide, GaAs, each Ga atom contributes three electrons and each As atom contributes five, which averages out to four per atom—the same number as in silicon or germanium. Hence, GaAs is a semiconductor. Other examples are InP, where indium contributes three valence electrons and phosphorus contributes five, and CdTe, where cadmium provides two valence electrons and tellurium contributes six. In both cases, the average is again four valence electrons per atom. GaAs, InP, and CdTe all crystallize with a zinc blende structure.

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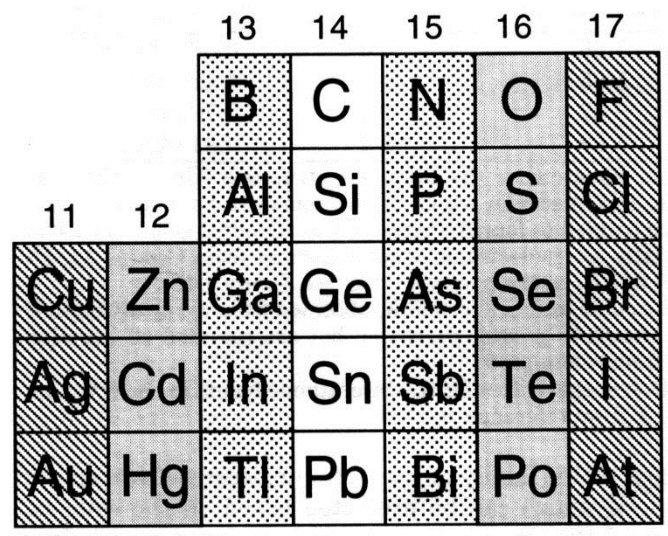
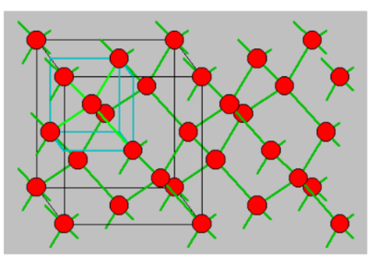
TABLE 12.4 Band Gaps of Select Elemental and Compound Semiconductors

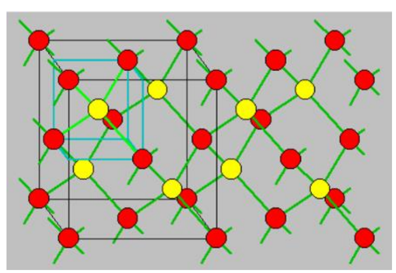
Material	Structure Type	E_g, eV†
Si	Diamond	1.11
AlP	Zinc blende	2.43
Ge	Diamond	0.67
GaAs	Zinc blende	1.43
ZnSe	Zinc blende	2.58
Sn‡	Diamond	0.08
InSb	Zinc blende	0.18
CdTe	Zinc blende	1.50



Diamond Lattice



The zinc-blende lattice of GaAs and InP

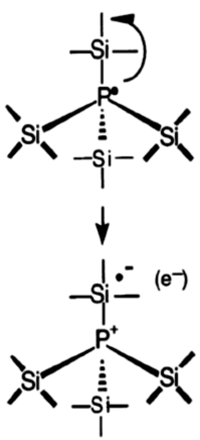


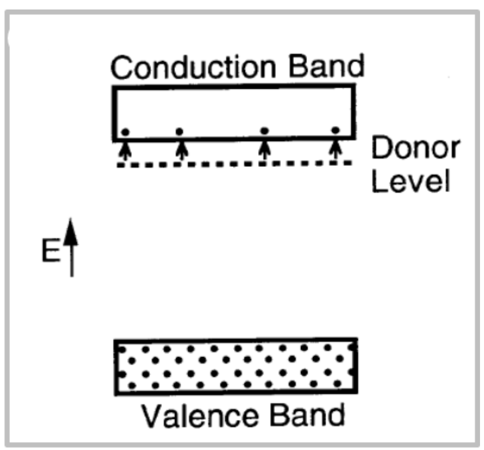
AZ solids having zinc blende structure and iso-electronic with the Group 14 solids are semiconductors. Complementary pairs are indicated with similar shading; e.g. Ge, GaAs, ZnSe, and CuBr.)

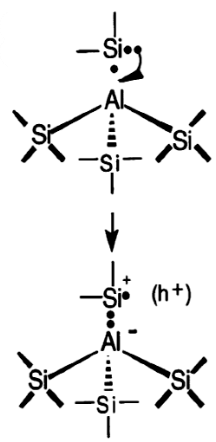
Review **Intrinsic** Semiconductors have a fixed band gap

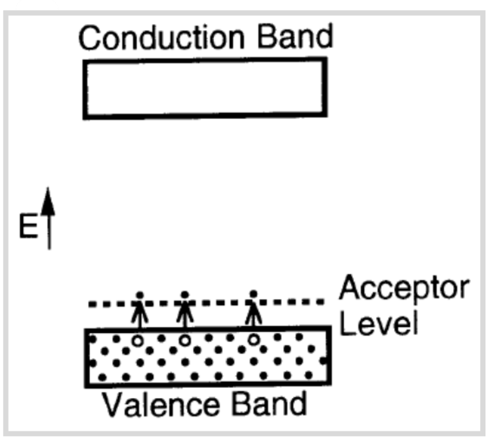
Element	C	Si	Ge	α-Sn
E_g/eV	5.47	1.11	0.66	< 0.1
(λ, nm)	(2300	1100	1900	12,000)

Extrinsic Semiconductors—trace amount of a dopant can make a dramatic change in conductivity









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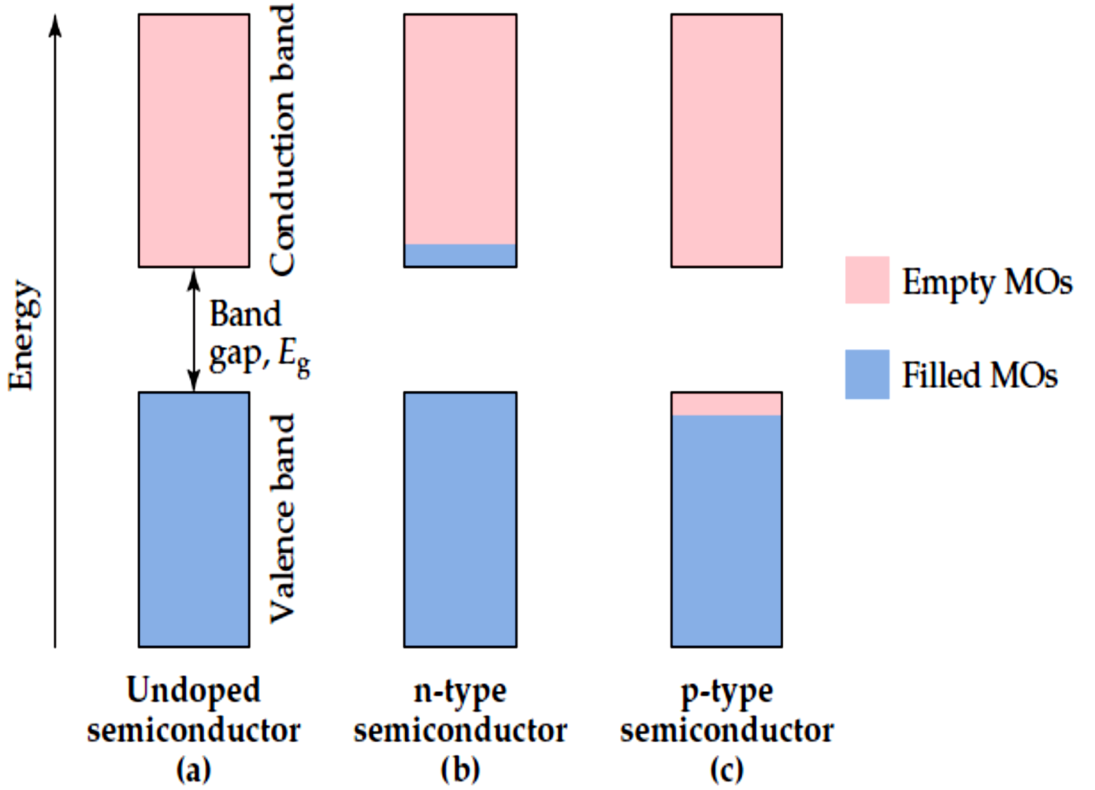
Through doping, it can make *n*-type or *p*-type extrinsic semiconductors.



▲ Figure 12.31 The addition of small amounts of impurities (doping) to a semiconductor changes the electronic properties of the material.

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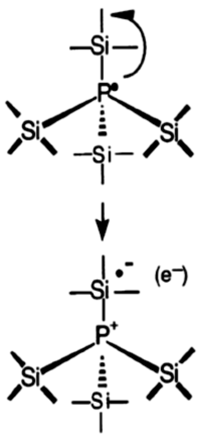
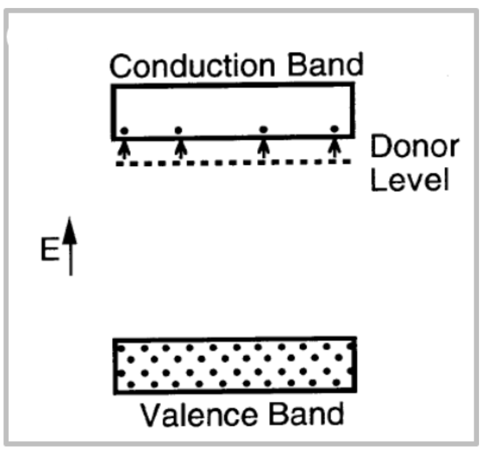
$$\mathrm{Si}_{\,(crystal)} \rightarrow h^{+} + e^{-}$$

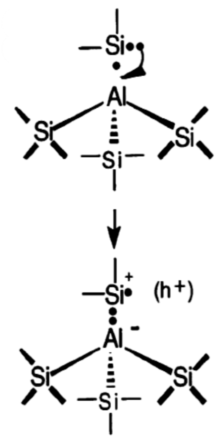
$$K = [h^{+}][e^{-}] = p \times n$$

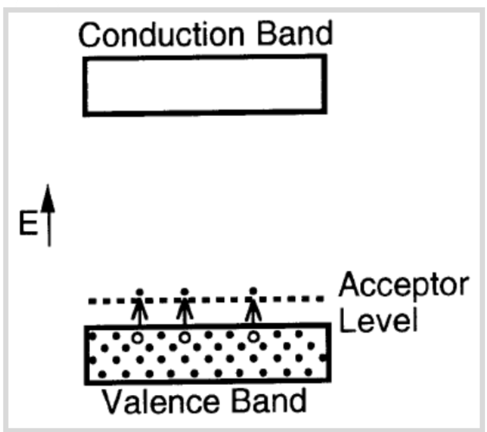
$$[h^{+}] \approx 1.5 \times 10^{10}\ \mathrm{cm}^{-3}$$

intrinsic density n_i : $p = n$









n*-type: *n* > *p

p*-type: *p* > *n

Exercise

A sample of silicon is doped with 10^{16} /cm^3 of Arsenic (As), group 15 atom. What are the concentrations of electrons and holes?

A sample of silicon is doped with $4x10^{16}$ /cm^3 of Gallium (Ga), a group 13 atom. What are the concentrations of electrons and holes?

A sample of silicon is doped with $3x10^{16}$ /cm^3 of Phosphorous and $6x10^{16}$ /cm^3 of Boron

What type is the material, what are the concentrations of electrons and holes, and which are the majority and minority carriers?

Review

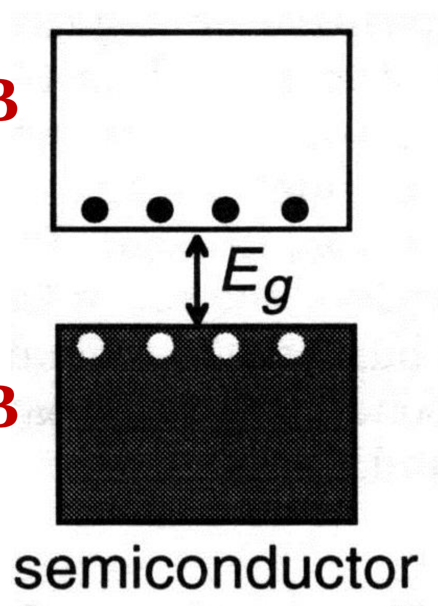
Intrinsic Semiconductors have a fixed band gap

Material	Cubic Unit-Cell Parameter, Å	$\Delta\chi$	E_g, eV (λ, nm)	
Ge	5.66	0.0	0.66 (1900)	B
GaAs	5.65 *	0.4	1.42 (890)	B
ZnSe	5.67	0.8	2.70 (460)	Y
CuBr	5.69	0.9	2.91 (430)	W

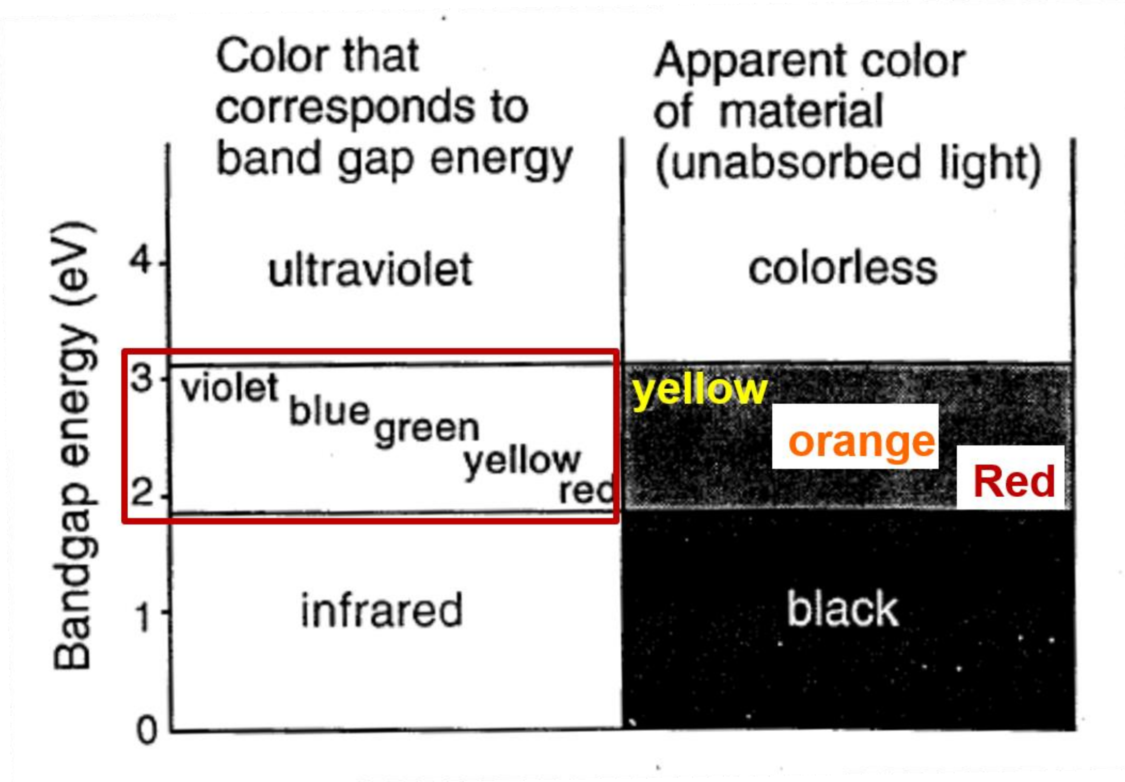
The band gap is a very important property of a semiconductor because it determines its color and conductivity.

CB

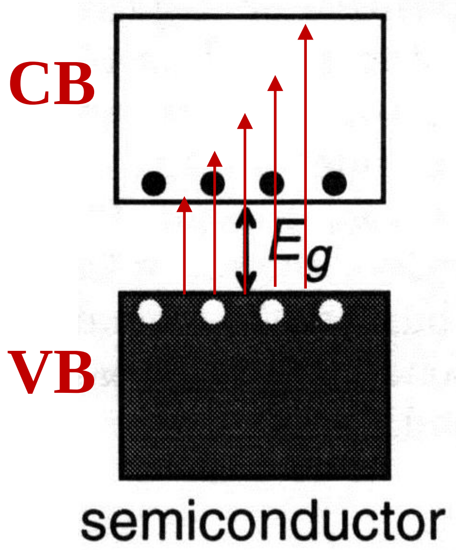
VB



The color of **absorbed** and **emitted** light both depend on the band gap of the semiconductor.



Visible light covers the range of approximately 390-700 nm, or 1.8 - 3.1 eV).



The color of absorbed light includes the band gap energy, but also all colors of higher energy (shorter wavelength), because electrons can be excited from the valence band to a range of energies in the conduction band. Thus

The color of **absorbed** and **emitted** light both depend on the band gap of the semiconductor.

Thus semiconductors with band gaps in the infrared (e.g., **Si**, 1.1 eV and **GaAs**, 1.4 eV) appear black because they absorb all colors of visible light.

Wide band gap semiconductors such as **TiO_2** (3.0 eV) are white because they absorb only in the UV.

Fe_2O_3 has a band gap of 2.2 eV and thus absorbs light with $\lambda < 560$ nm. It thus appears reddish-orange (the colors of light reflected from Fe_2O_3) because it absorbs yellow, green, blue, and violet light.

Fe_2O_3 powder is reddish orange because of its 2.2 eV band gap.

Similarly, **CdS** ($E_g = 2.6$ eV) is yellow because it absorbs blue and violet light.

Compound semiconductors with a type of **electron conduction** determined by the stoichiometry

-type conduction							
BaO	TiO_2	V_2O_8	MoO_2	Fe_3O_4	Ag_2S	$BaTiO_3$	$PbCrO_4$
Cs_2S	Cs_2Se	Nb_2O_5	WO_3	Hg_2S	ZnO	CdS	SnO_2
-type conduction							
Cr_2O_3	Pr_2O_3	MnO	CoO	NiO	SnO	Cu_2O	Cu_2S
Bi_2Te_3	MoO_2	Hg_2O	Sb_2S_3	Ag_2O	SnS	CuI	
Amphoteric conduction							
Al_2O_3	SiC	Mn_3O_4	Co_3O_4	Ti_2S	PbS	$PbSe$	$PbTe$

Because the wavelength of light that is emitted depends on the band gap of the semiconductor, the color of light produced by the LED can be controlled by appropriate choice of semiconductor. Most **red LEDs** are made of **a mixture of GaP and GaAs**. The band gap of GaP is 2.26 eV (3.62×10^{-19} J), which corresponds to a green photon with a wavelength of 549 nm, while GaAs has a band gap of 1.43 eV (2.29×10^{-19} J), which corresponds to an infrared photon with a wavelength of 867 nm.

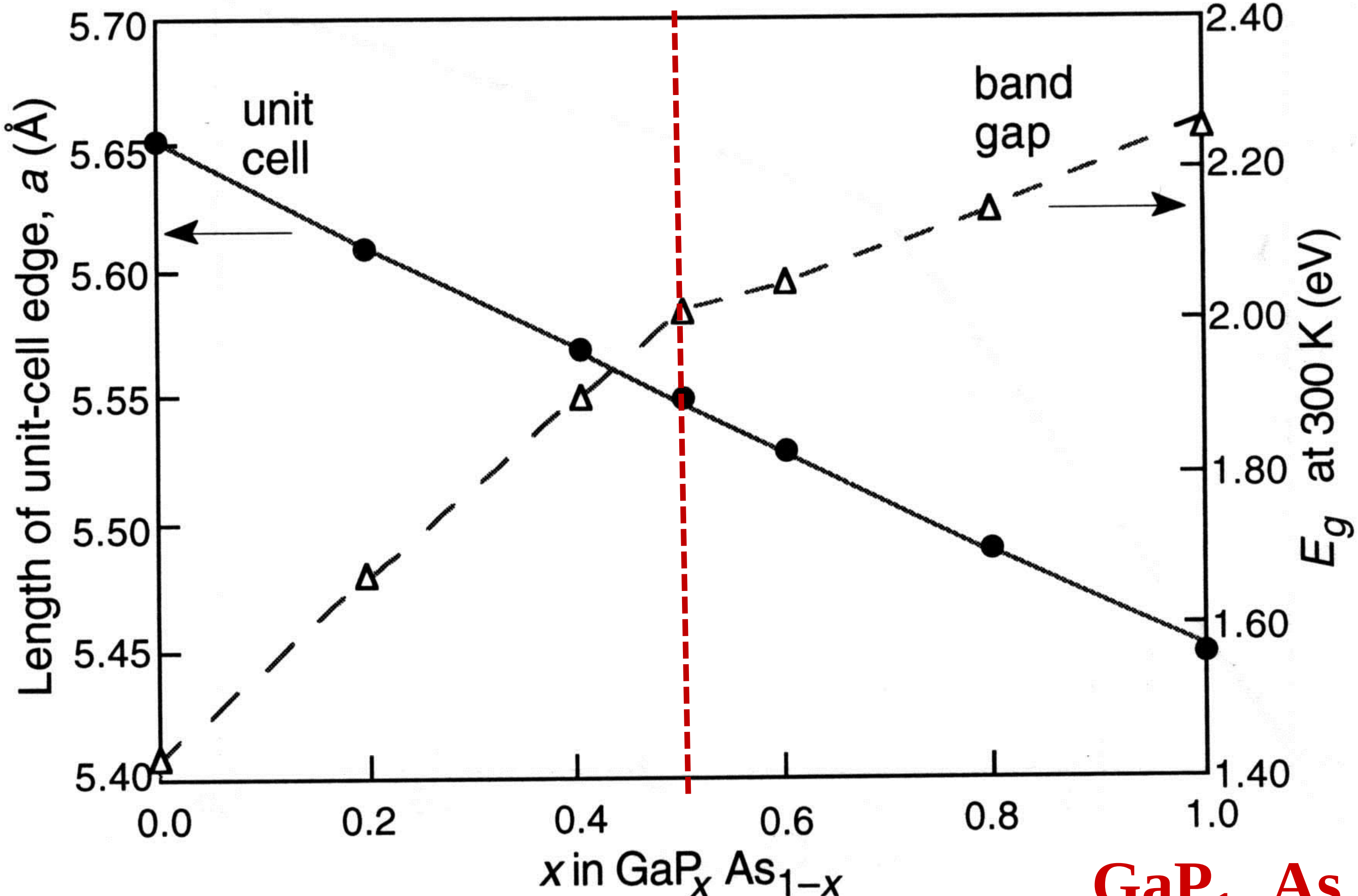
By forming solid solutions of these two compounds, with stoichiometries of $GaP_{1-x}As_x$, the band gap can be adjusted to any intermediate value. Thus, $GaP_{1-x}As_x$ is the solid solution of choice for red, orange, and yellow LEDs. Green LEDs are made from mixtures of GaP and AlP (E_g = 2.43 eV, λ = 510 nm). Red LEDs have been in the market for decades, but to make white light, an efficient blue LED was needed. The first prototype bright blue LED was demonstrated in a Japanese laboratory in 1993. In 2010, less than 20 years later, over $10 billion worth of blue LEDs were sold worldwide. The blue LEDs are based on combinations of GaN (E_g = 3.4 eV, λ = 365 nm) and InN (E_g = 2.4 eV, λ = 517 nm). Many colors of LEDs are now available and are used in everything from barcode scanners to traffic lights. Because the light emission results from semiconductor structures that can be made extremely small and because they emit little heat, LEDs are replacing standard incandescent and fluorescence light bulbs in many applications.

Review **Solid Solutions Having the Zinc Blende Structure**

GaP_xAs_{1-x} $(1 \geq x \geq 0)$

GaAs: E_g=1.4 eV

GaP: E_g=2.3 eV

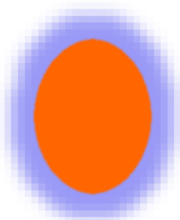


$GaP_{1-y}As_y$

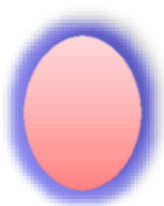
The kink in the band gap at x = 0.45 corresponds to a change from a direct band gap to an indirect band gap. Direct band gap materials absorb light strongly at band-gap energy and emit band-gap energy light with high efficiency. **Indirect band gap** materials absorb light more weakly and yield less efficient radioactive recombination (inferior LED materials).

Temperature Effect: plunging an LED into liquid nitrogen

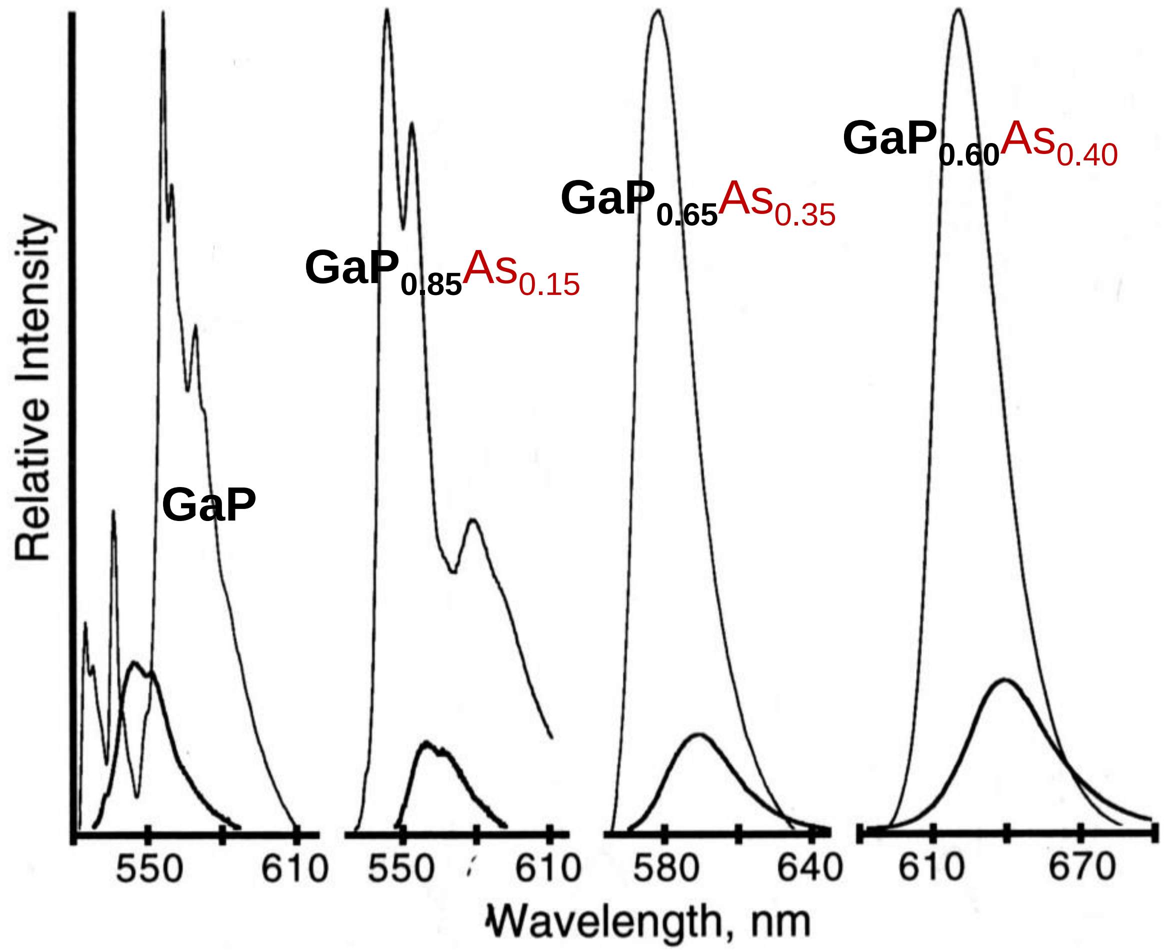
bright orange



77 K



300 K



Spectra of GaP_xAs_{1-x} LEDs at 300 K (thicker lines) and at 77K (thinner lines). Data for GaP: a = 5.451 Å and E_g=2.27 eV (λ = 550 nm) at 300 K and a= 5.447 Å and E_g=2.33 eV (λ = 530 nm) at 77 K.

Review

Type	Examples	Structural Units	Forces Holding Units Together
Ionic	$NaCl$, K_2SO_4, $CaCl_2$, $(NH_4)_3PO_4$	Positive and negative ions; no discrete molecules	Ionic; attractions among charges on positive and negative ions
Metallic	Iron, silver, copper, other metals and alloys	Metal atoms (positive metal ions with delocalized electrons)	Metallic; electrostatic attraction among metal ions and electrons
Molecular	H_2, O_2, I_2, H_2O, CO_2, CH_4, CH_3OH, CH_3CO_2H	Molecules	Dispersion forces, dipole–dipole forces, hydrogen bonds
Network	Graphite, diamond, quartz, feldspars, mica	Atoms held in an infinite two- or three-dimensional network	Covalent; directional electron-pair bonds
Amorphous	Glass, polyethylene, nylon	Covalently bonded networks with no long-range regularity	Covalent; directional electron-pair bonds