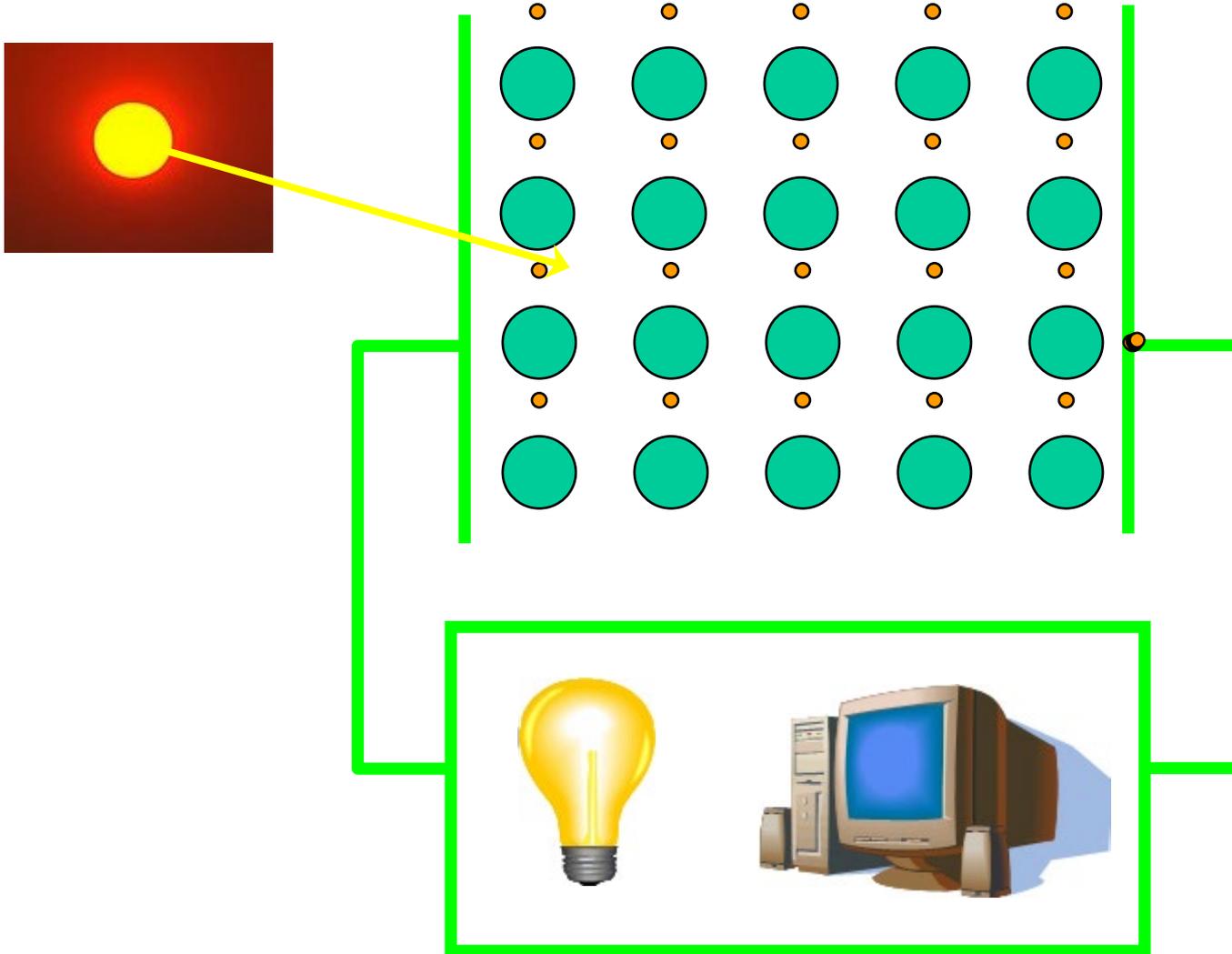


# **Lecture 3**

## **Introduction to Semiconductors and Energy Bandgaps**

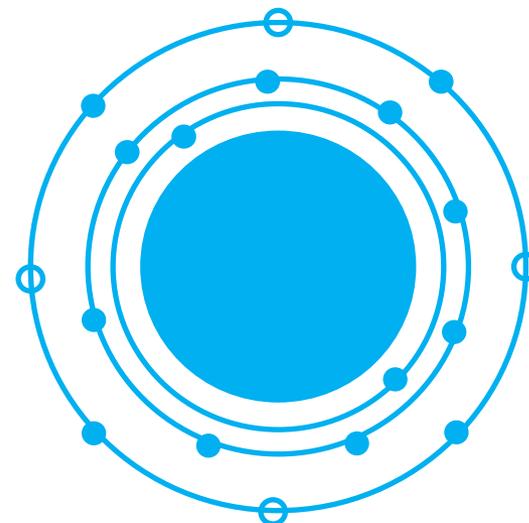
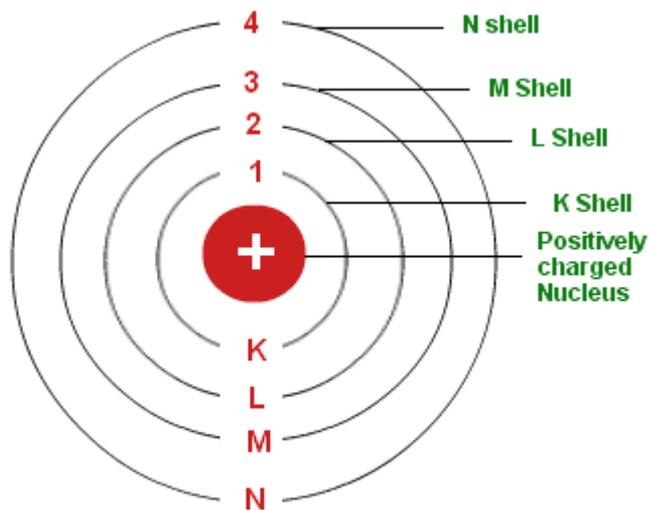
# Solar Cells



Why do the electrons flow when light is present but not flow when light is not present?

Answer, Energy Bandgap (very important concept).

# Classifications of Electronic Materials

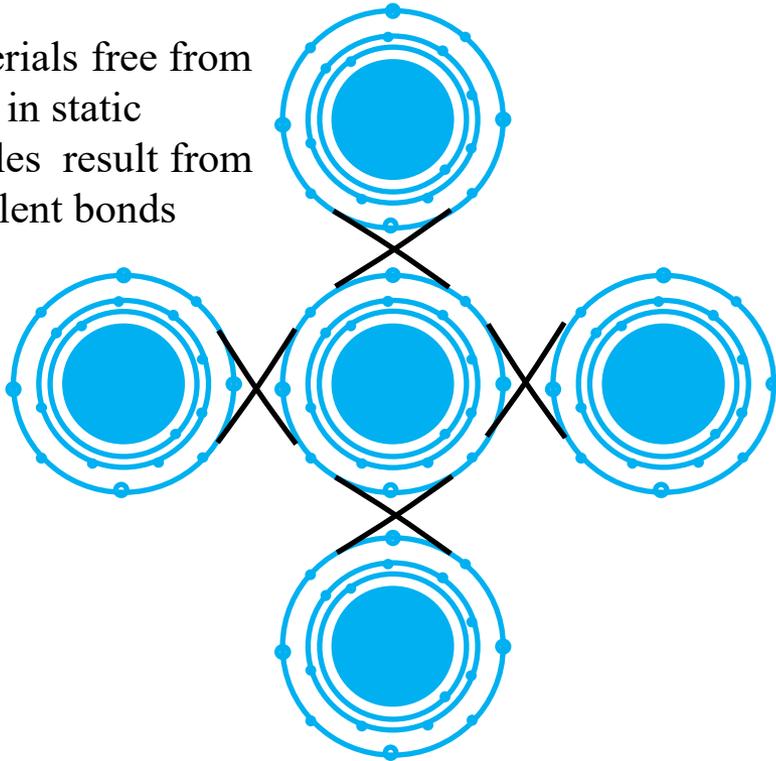


Example: Silicon  $n=1$  (2 s),  $n=2$  (2 s and 6 p) and  $n=3$  (2 s and 2 p with 4 unoccupied p states)

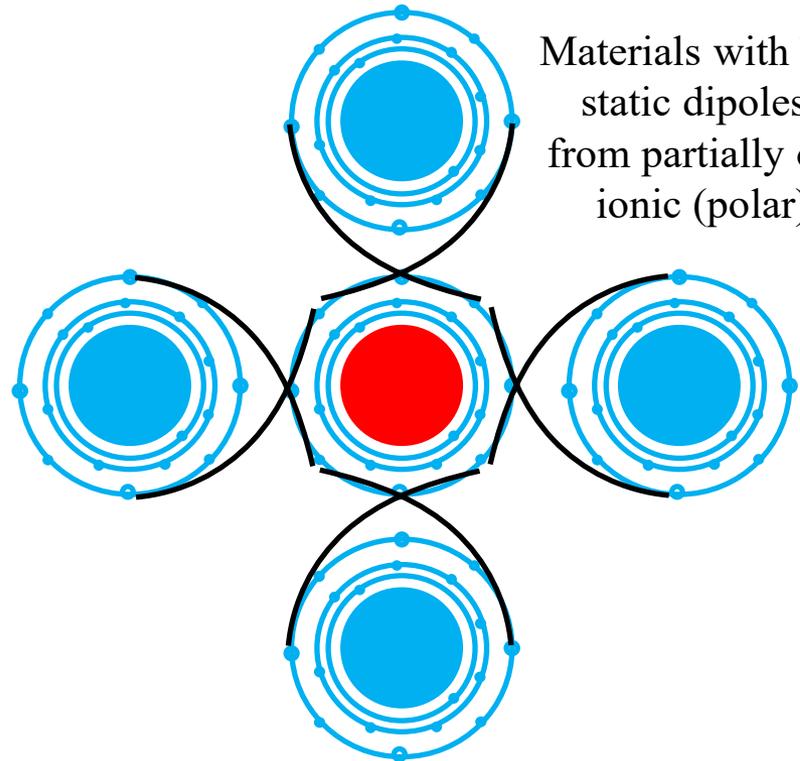
- Atoms contain various “orbitals”, “levels” or “shells” of electrons labeled as  $n=1, 2, 3, 4, \text{etc.}$  or K, L, M, or N etc... The individual allowed electrons “states” are simply allowed positions (energy and space) within each orbital/level/shell for which an electron can occupy.
- Electrons fill up the levels (fill in the individual states in the levels) from the smallest  $n$  shell to the largest occupying “states” (available orbitals) until that orbital is completely filled then going on to the next higher orbital.
- The outer most orbital/level/shell is called the “Valence orbital”. This valence orbital is the only one that participated in the bonding of atoms together to form solids.

# Classifications of Electronic Materials

Materials free from built in static dipoles result from covalent bonds

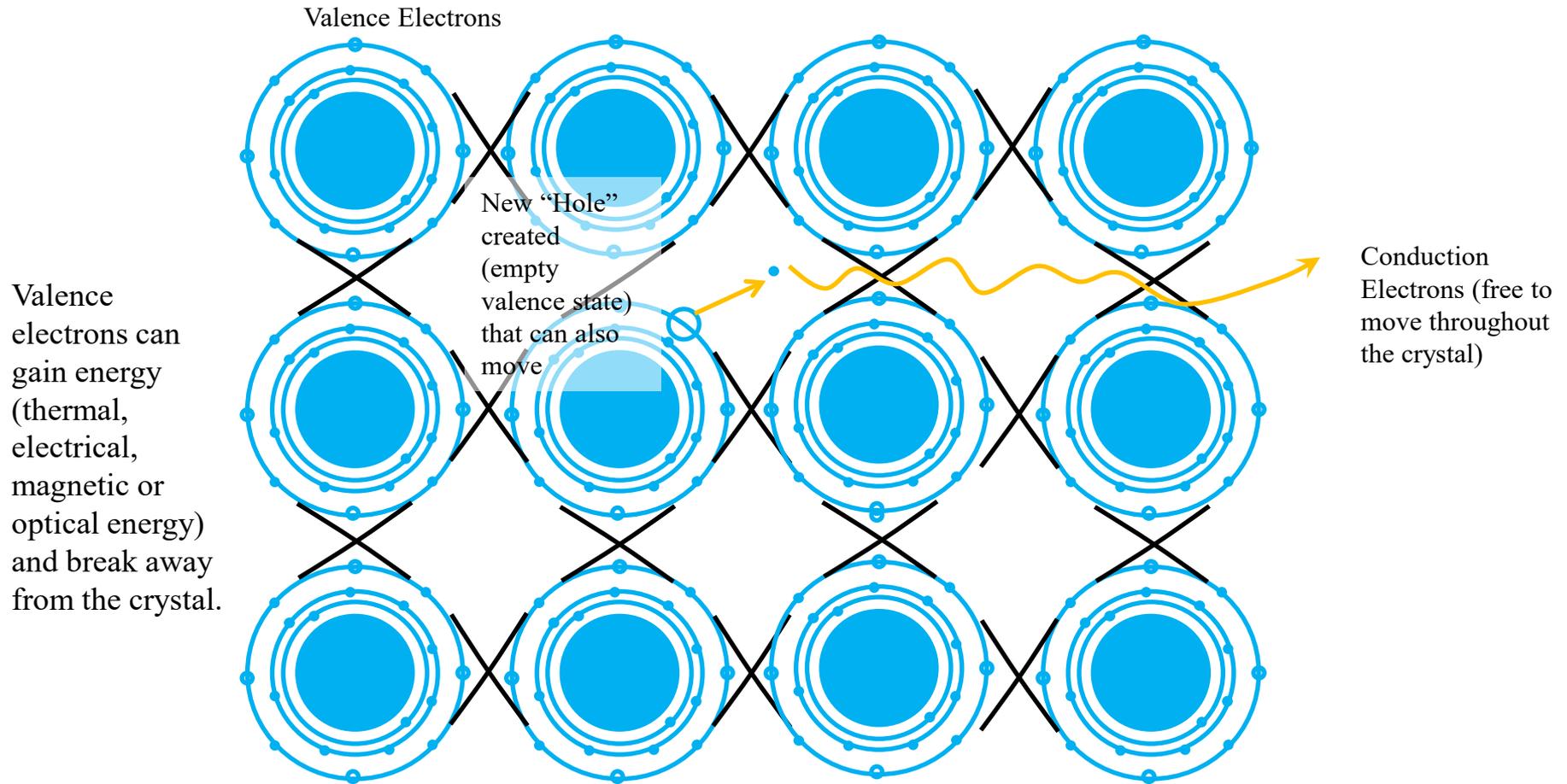


Materials with built in static dipoles result from partially or fully ionic (polar) bonds



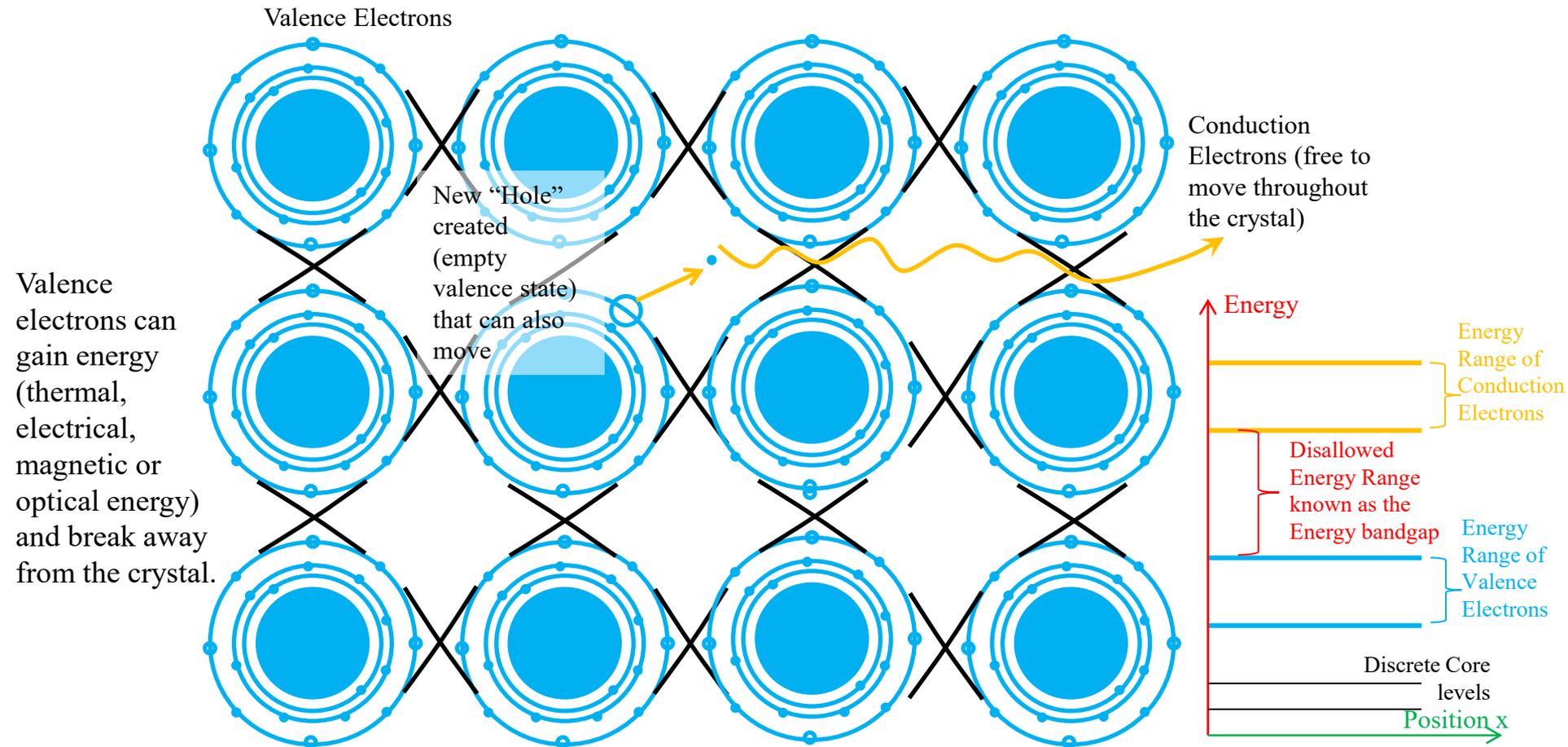
- Solids are formed by several methods, including (but not limited to) sharing electrons (covalent bonds) or by columbic attraction of ions (fully ionic) or partial ionic attraction / partial sharing of electrons (partially ionic)
- The method for which the semiconductor forms, particularly whether or not a fixed static di-pole is constructed inside the crystal, effects the way the semiconductor interacts with light.
- Later we will see that covalent bonds tend toward “indirect bandgap” (defined later) materials whereas polar bonds (ionic and partially ionic) tend toward “direct bandgap” materials.

# Classifications of Electronic Materials



- Only the outermost core levels participate in bonding. We call these "Valence orbits" or "Valence Shells".
- For metals, the electrons can jump from the valence orbits (outermost core energy levels of the atom) to any position within the crystal (free to move throughout the crystal) with no "extra energy needed to be supplied". Thus, "free conducting electrons are prevalent at room temperature.
- For insulators, it is VERY DIFFICULT for the electrons to jump from the valence orbits and requires a huge amount of energy to "free the electron" from the atomic core. Thus, few conducting electrons exist.
- For semiconductors, the electrons can jump from the valence orbits but does require a small amount of energy to "free the electron" from the atomic core, thus making it a "**SEMI**-conductor".

# Classifications of Electronic Materials



• Since the electrons in the valence orbitals of a solid can have a range of energies and since the free conducting electrons can have a range of energies, semiconductor materials are a sub-class of materials distinguished by the existence of a range of disallowed energies between the energies of the valence electrons (outermost core electrons) and the energies of electrons free to move throughout the material.

• The energy difference (**energy gap or bandgap**) between the states in which the electron is bound to the atom and when it is free to conduct throughout the crystal is related to the bonding strength of the material, its density, the degree of ionicity of the bond, and the chemistry related to the valence of bonding.

• High bond strength materials (diamond, SiC, AlN, GaN etc...) tend to have large energy bandgaps.

• Low bond strength materials (Si, Ge, InSb, etc...) tend to have smaller energy bandgaps.

# Classifications of Electronic Materials

- More formally, the energy gap is derived from the Pauli exclusion principle, where no two electrons occupying the same space, can have the same energy. Thus, as atoms are brought closer towards one another and begin to bond together, their energy levels must split into bands of discrete levels so closely spaced in energy, they can be considered a continuum of allowed energy.
- Strongly bonded materials tend to have small interatomic distances between atoms. Thus, the strongly bonded materials can have larger energy bandgaps than do weakly bonded materials.

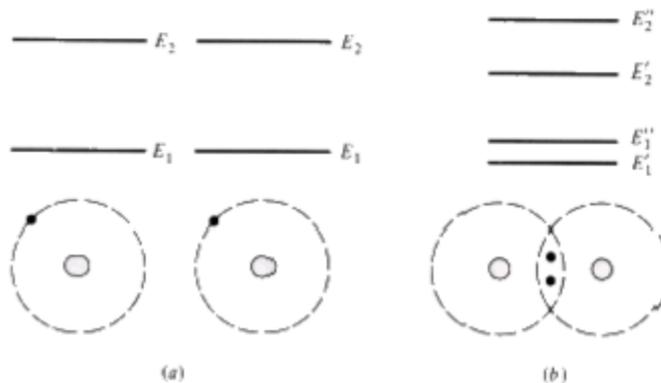
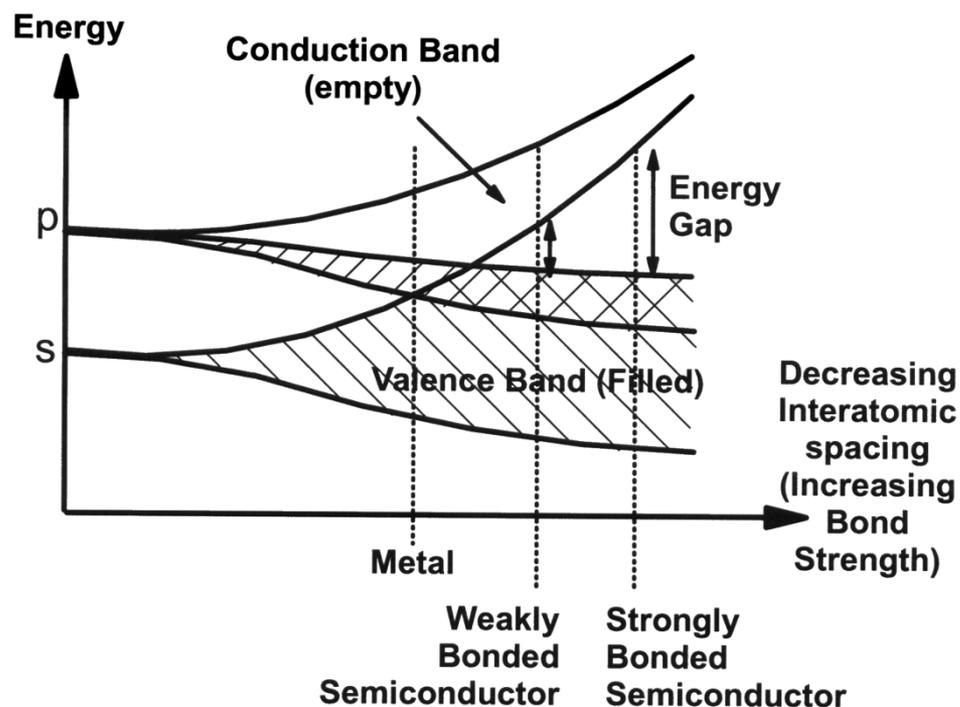
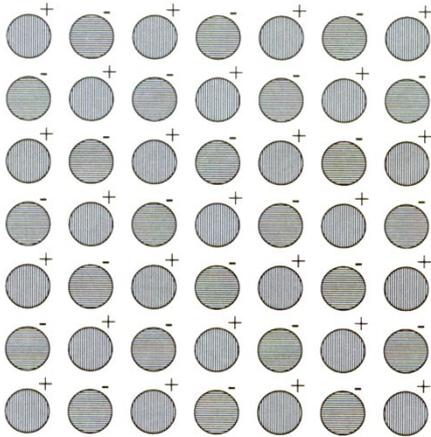


FIGURE 1-9 Two hydrogen atoms: (a) noninteracting and (b) interacting. Splitting of energy levels is illustrated for (b).

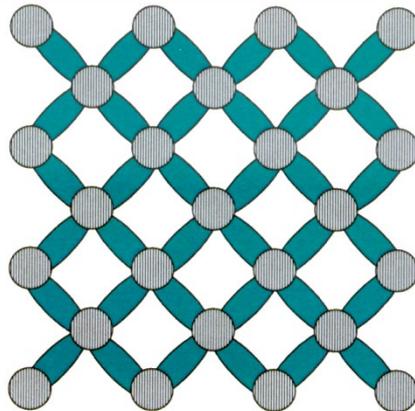


# Material Classifications based on Bonding Method

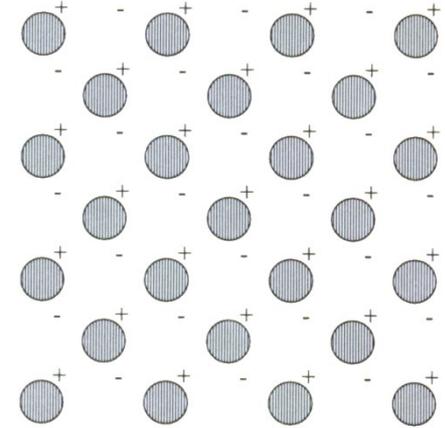
Bonds can be classified as metallic, Ionic, Covalent, and van der Waals.



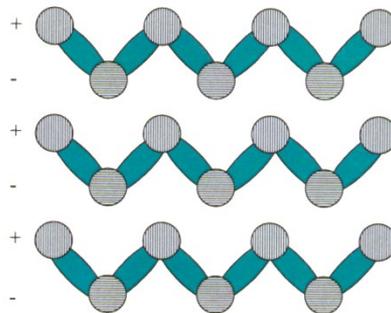
**Ionic Bonding:** One atom acquires and holds the electron(s) of an adjacent atom. Bonding is coulombic and strong.



**Covalent Bonding:** Atoms share electrons with the surrounding atoms. Bonding is moderately weak.



**Metallic Bonding:** Atoms give up electrons to the surrounding regions, forming an “electron cloud”. Bonding is coulombic but weak due to screening of charge.



**Van der Waals Bonding:** Neutrally charged molecules form dipoles which are attracted to other dipoles. Bonding is extremely weak, but long chains can form.

# Consider the case of the group 4 elements, all\*\* covalently bonded

Element Atomic Radius/Lattice Constant Bandgap

(How closely spaced are the atoms?)

C	0.91/3.56 Angstroms	5.47 eV
Si	1.46/5.43 Angstroms	1.12 eV
Ge	1.52/5.65 Angstroms	0.66 eV
$\alpha$ -Sn	1.72/6.49 Angstroms	~0.08 eV*
Pb	1.81/** Angstroms	Metal

**ELEMENTS**

Selected Radioactive Isotopes

Naturally occurring radioactive isotopes are designated by a mass number in this (although some are also manufactured). Letter in parentheses follows in parentheses, where x, min. h, d, and y stand respectively for seconds, minutes, hours, days, and years. The table includes many of the longest-lived radioactive isotopes, many others have been prepared, isotopes known to be radioactive but with half-lives exceeding 10<sup>10</sup> years not being included. Symbols describing the principal mode (or modes) of decay are as follows: these processes are generally accompanied by gamma radiation:

- $\alpha$  alpha particle emission
- $\beta^-$  beta particle (electron) emission
- $\beta^+$  positron emission
- EC orbital electron capture
- IT isomeric transition from upper to lower isomeric state
- SF spontaneous fission

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# Classifications of Electronic Materials

## Types of Semiconductors:

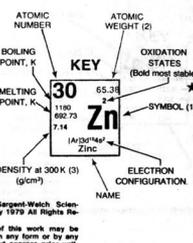
- Elemental: Silicon or Germanium (Si or Ge)
- Compound: Gallium Arsenide (GaAs), Indium Phosphide (InP), Silicon Carbide (SiC), CdS and many others

•Note that the sum of the valence adds to 8, a complete outer shell. I.E. 4+4, 3+5, 2+6, etc...

## PERIODIC TABLE OF THE ELEMENTS

Table of Selected Radioactive Isotopes

GROUP IA		GROUP IIA		GROUP IIIA to VIIA										GROUP VIII			
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 1.00794 H Hydrogen	2 4.00260 He Helium	3 6.941 Li Lithium	4 9.01218 Be Beryllium	5 9.01218 B Boron	6 12.011 C Carbon	7 14.007 N Nitrogen	8 15.999 O Oxygen	9 18.998 F Fluorine	10 20.179 Ne Neon	11 22.989 Na Sodium	12 24.305 Mg Magnesium	13 26.981 Al Aluminum	14 28.085 Si Silicon	15 30.974 P Phosphorus	16 32.06 S Sulfur	17 35.453 Cl Chlorine	18 39.948 Ar Argon
19 39.098 K Potassium	20 40.078 Ca Calcium	21 44.955 Sc Scandium	22 47.867 Ti Titanium	23 50.941 V Vanadium	24 51.996 Cr Chromium	25 54.938 Mn Manganese	26 55.845 Fe Iron	27 58.933 Co Cobalt	28 58.933 Ni Nickel	29 63.546 Cu Copper	30 65.38 Zn Zinc	31 69.723 Ga Gallium	32 72.59 Ge Germanium	33 74.921 As Arsenic	34 78.96 Se Selenium	35 79.904 Br Bromine	36 83.80 Kr Krypton
37 85.467 Rb Rubidium	38 87.62 Sr Strontium	39 88.905 Y Yttrium	40 91.224 Zr Zirconium	41 92.906 Nb Niobium	42 95.94 Mo Molybdenum	43 98.04 Tc Technetium	44 101.07 Ru Ruthenium	45 102.905 Rh Rhodium	46 106.42 Pd Palladium	47 107.868 Ag Silver	48 112.411 Cd Cadmium	49 114.818 In Indium	50 118.710 Sn Tin	51 121.757 Sb Antimony	52 127.6 Te Tellurium	53 126.905 I Iodine	54 131.30 Xe Xenon
55 132.905 Cs Cesium	56 137.33 Ba Barium	57 138.905 La Lanthanum	72 178.48 Hf Hafnium	73 180.947 Ta Tantalum	74 183.85 W Tungsten	75 186.207 Re Rhenium	76 190.23 Os Osmium	77 192.22 Ir Iridium	78 195.084 Pt Platinum	79 196.967 Au Gold	80 200.59 Hg Mercury	81 204.37 Tl Thallium	82 207.2 Pb Lead	83 208.980 Bi Bismuth	84 (209) Po Polonium	85 (210) At Astatine	86 (222) Rn Radon
87 (223) Fr Francium	88 (226) Ra Radium	89 (227) Ac Actinium	104 (261) Uuq (Unnilquadium)	105 (262) Uup (Unnilpentium)	106 (263) Uuh (Unnilhexium)	<p>† The names and symbols of elements 104 - 106 are those recommended by IUPAC on systematic alternatives to those suggested by the proposed discoverers. Backer (USA) researchers have proposed Uuq, Uup, and Uuh for elements 104 and 105 and the discovery of these elements have proposed different names (and symbols).</p>											



58	59	60	61	62	63	64	65	66	67	68	69	70	71	72
Ce Cerium	Pr Praseodymium	Nd Neodymium	Pm Promethium	Sm Samarium	Eu Europium	Gd Gadolinium	Tb Terbium	Dy Dysprosium	Ho Holmium	Er Erbium	Tm Thulium	Yb Ytterbium	Lu Lutetium	
90	91	92	93	94	95	96	97	98	99	100	101	102	103	104
Th Thorium	Pa Protactinium	U Uranium	Np Neptunium	Pu Plutonium	Am Americium	Cm Curium	Bk Berkelium	Cf Californium	Es Einsteinium	Fm Fermium	Md Mendelevium	No Nobelium	Lr Lawrencium	

The A & B subgroup designations, applicable to elements in rows 4, 5, 6, and 7, are those recommended by the International Union of Pure and Applied Chemistry. It should be noted that some authors and organizations use the opposite convention in distinguishing these subgroups.

# Classifications of Electronic Materials

Compound Semiconductors: Offer high performance (optical characteristics, higher frequency, higher power) than elemental semiconductors and greater device design flexibility due to mixing of materials.

Binary: GaAs, SiC, etc...

Ternary:  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ,  $\text{In}_x\text{Ga}_{1-x}\text{N}$  where  $0 \leq x \leq 1$

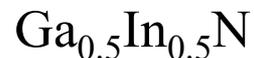
Quaternary:  $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$  where  $0 \leq x \leq 1$  and  $0 \leq y \leq 1$

Half the total number of atoms must come from group III (Column III) and the other half the atoms must come from group V (Column V) (or more precisely, IV/IV, III/V, or II/VI combinations) leading to the above “reduced semiconductor notation.

Example: Assume a compound semiconductor has 25% “atomic” concentrations of Ga, 25% “atomic” In and 50% “atomic” of N. The chemical formula would be:



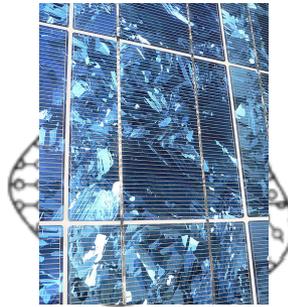
But the correct reduced semiconductor formula would be:



# Classifications of Electronic Materials



(a) Amorphous  
No recognizable  
long-range order



(b) Polycrystalline  
Completely ordered  
in segments



(c) Crystalline  
Entire solid is made up of  
atoms in an orderly array

General classification of solids based on the degree of atomic order: (a) amorphous, (b) polycrystalline, and (c) crystalline.

Increasing  
structural  
quality and  
increasing  
efficiency  
(performance)

## Material Classifications based on Crystal Structure

### *Amorphous Materials*

No discernible long range atomic order (no detectable crystal structure). Examples are silicon dioxide ( $\text{SiO}_2$ ), amorphous-Si, silicon nitride ( $\text{Si}_3\text{N}_4$ ), and others. Though usually thought of as less perfect than crystalline materials, this class of materials is extremely useful.

### *Polycrystalline Materials*

Material consisting of several “domains” of crystalline material. Each domain can be oriented differently than other domains. However, within a single domain, the material is crystalline. The size of the domains may range from cubic nanometers to several cubic centimeters. Many semiconductors are polycrystalline as are most metals.

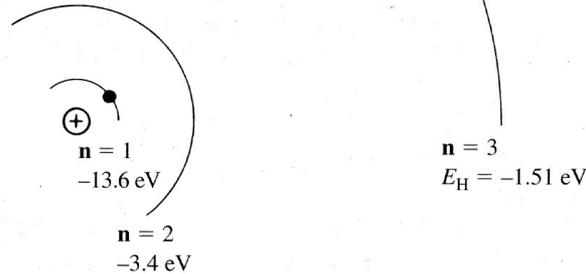
### *Crystalline Materials*

Crystalline materials are characterized by an atomic symmetry that repeats spatially. The shape of the unit cell depends on the bonding of the material. The most common unit cell structures are diamond, zincblende (a derivative of the diamond structure), hexagonal, and rock salt (simple cubic).

# **Chemical Bonding Determines the Bandgap**

# Comparison of the Hydrogen Atom and Silicon Atom

## Hydrogen



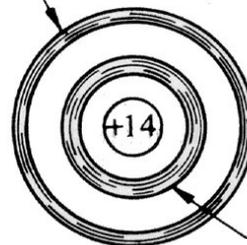
$$Energy_{Hydrogen\ electron} = -\frac{m_o q^4}{2(4\pi \epsilon_0 \hbar n)^2} = -\frac{13.6\ eV}{n^2}$$

where  $m_o$  = electron mass,  $\hbar$  = planks constant /  $2\pi = h / 2\pi$   
 $q$  = electron charge, and  $n = 1, 2, 3, \dots$

**Figure 2.1** The hydrogen atom—idealized representation showing the first three allowed electron orbits and the associated energy quantization.

n=2: Complete Shell  
 2 “2s electrons”  
 6 “2p electrons”  
 8 Electrons

## Silicon



n=3:  
 2 “3s electrons”  
 Only 2 of 6 “3p electrons”

**4 empty states**

**4 Valence Shell Electrons**

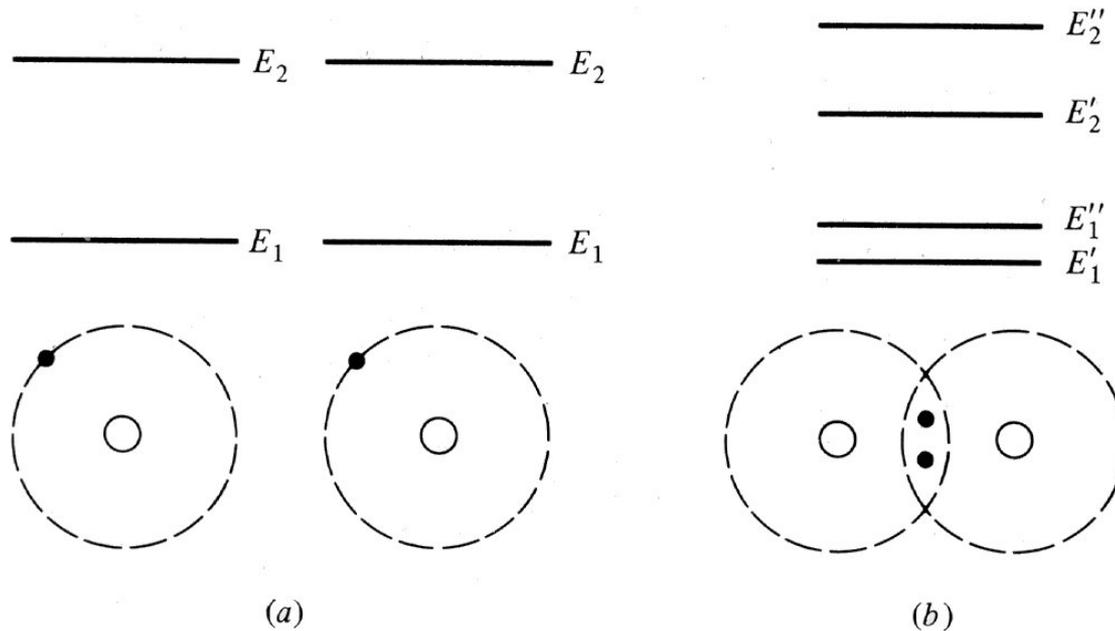
Six allowed levels at same energy

Two allowed levels at same energy

**Figure 2.2** Schematic representation of an isolated Si atom.

# Pauli Exclusion Principle

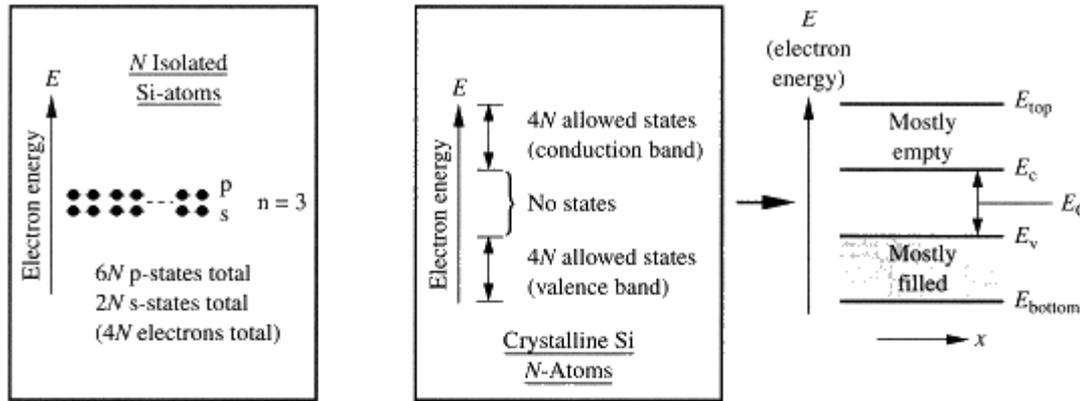
Only 2 electrons, of spin  $\pm 1/2$ , can occupy the same energy state at the same point in space.



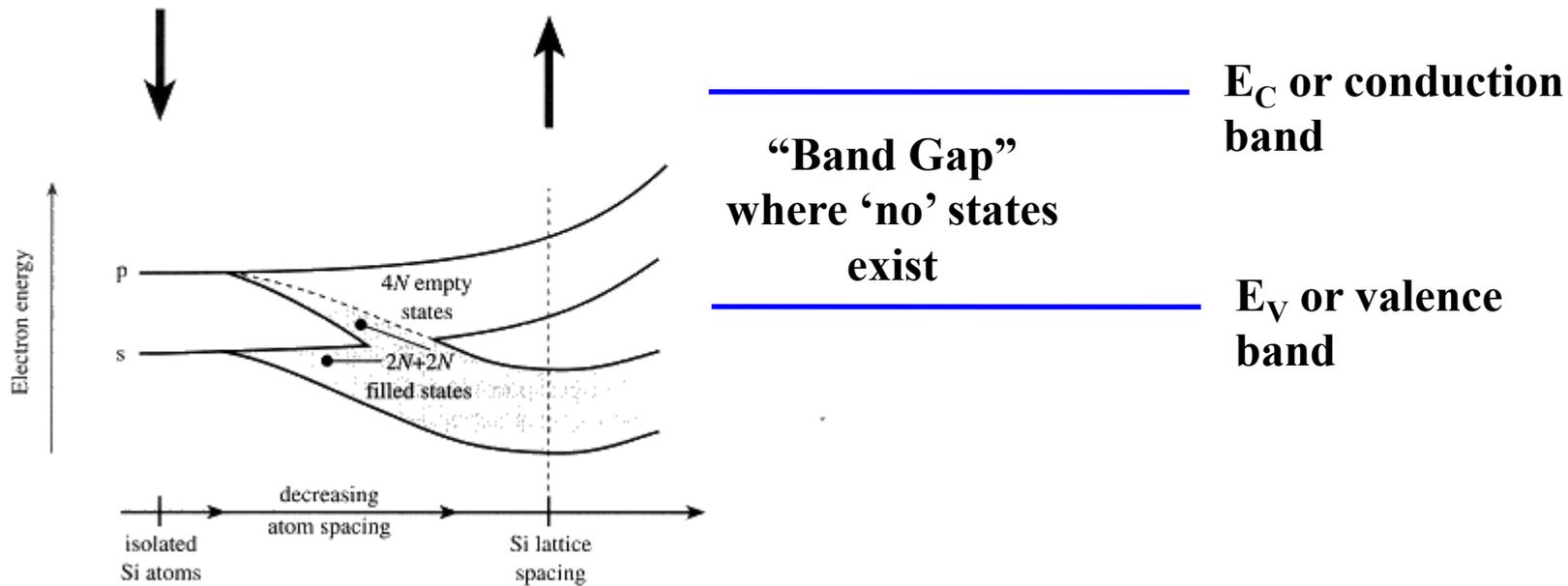
**FIGURE 1-9**

Two hydrogen atoms: (a) noninteracting and (b) interacting. Splitting of energy levels is illustrated for (b).

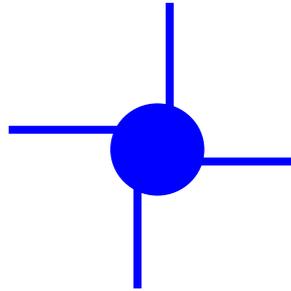
# Banding of Discrete states and the Simplified Model



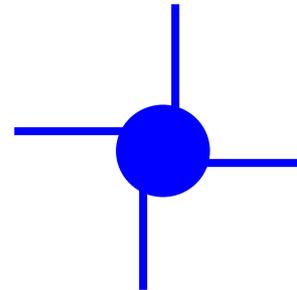
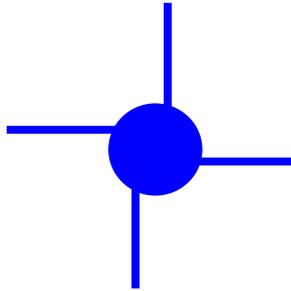
**T=0K**

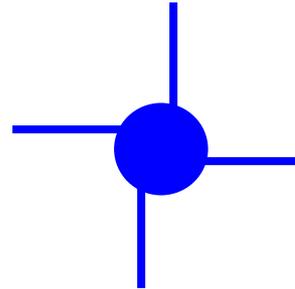
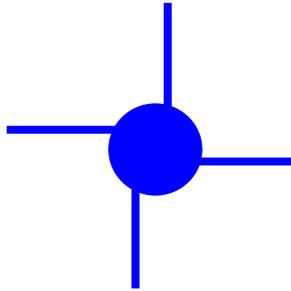


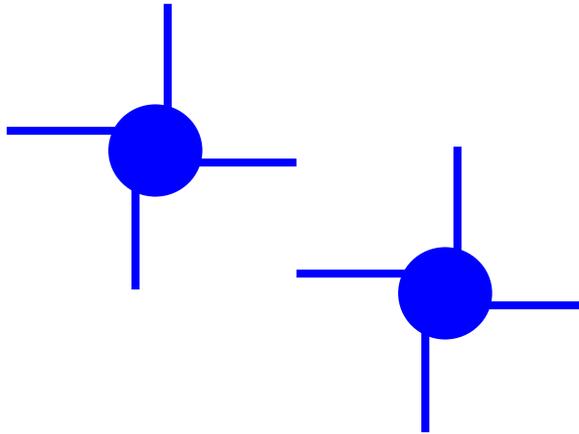
**Figure 2.5** Conceptual development of the energy band model starting with  $N$  isolated Si atoms on the top left and concluding with a “dressed-up” version of the energy band model on the top right.

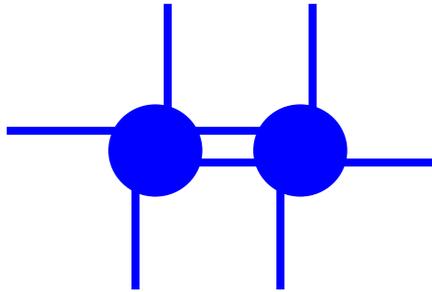


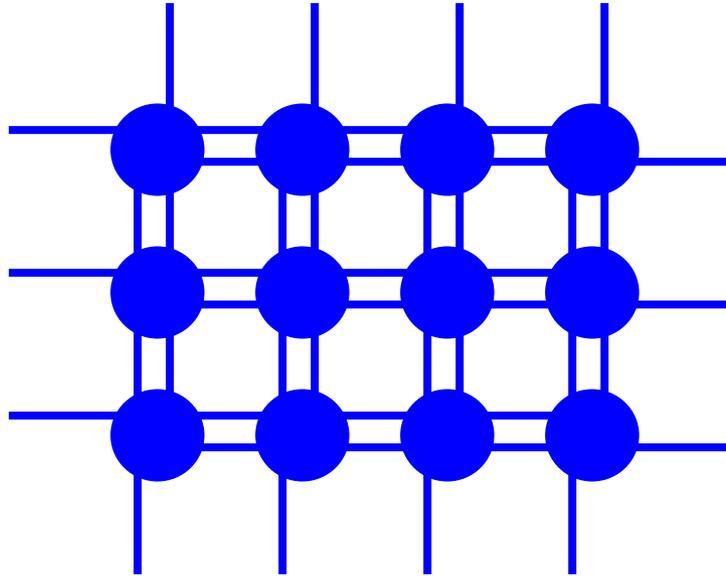
**4 electrons available for sharing  
(covalent bonding) in outer shell  
of atoms**

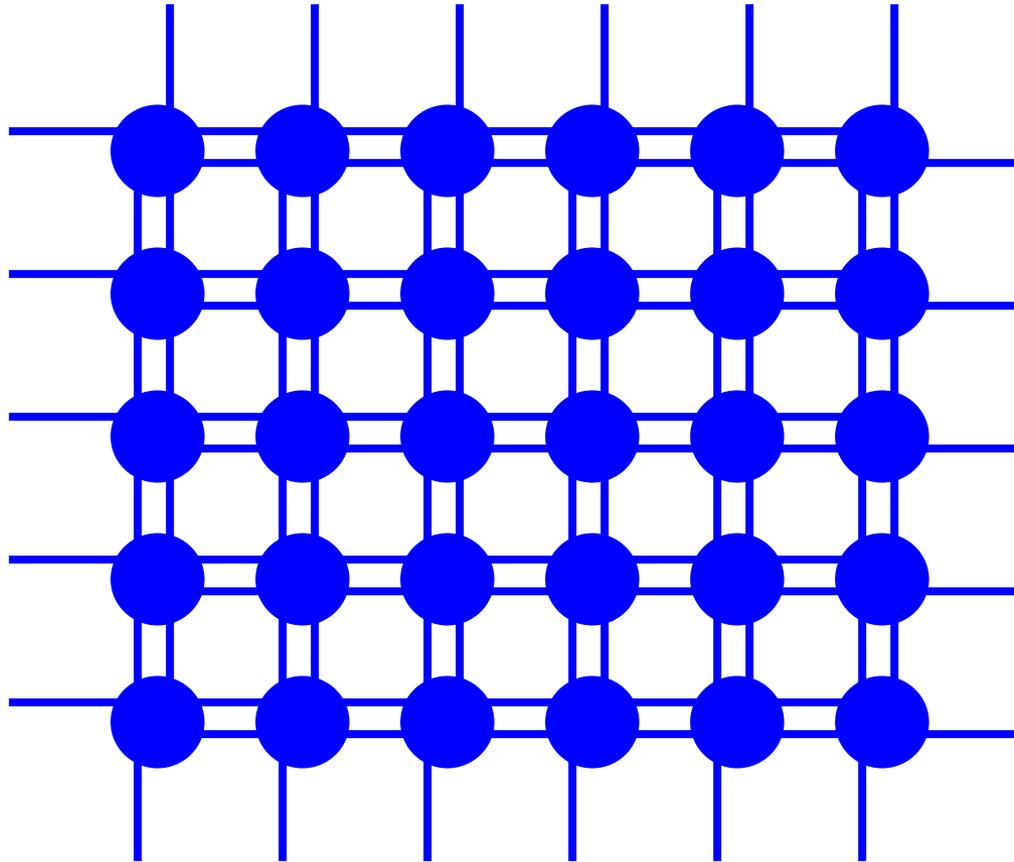


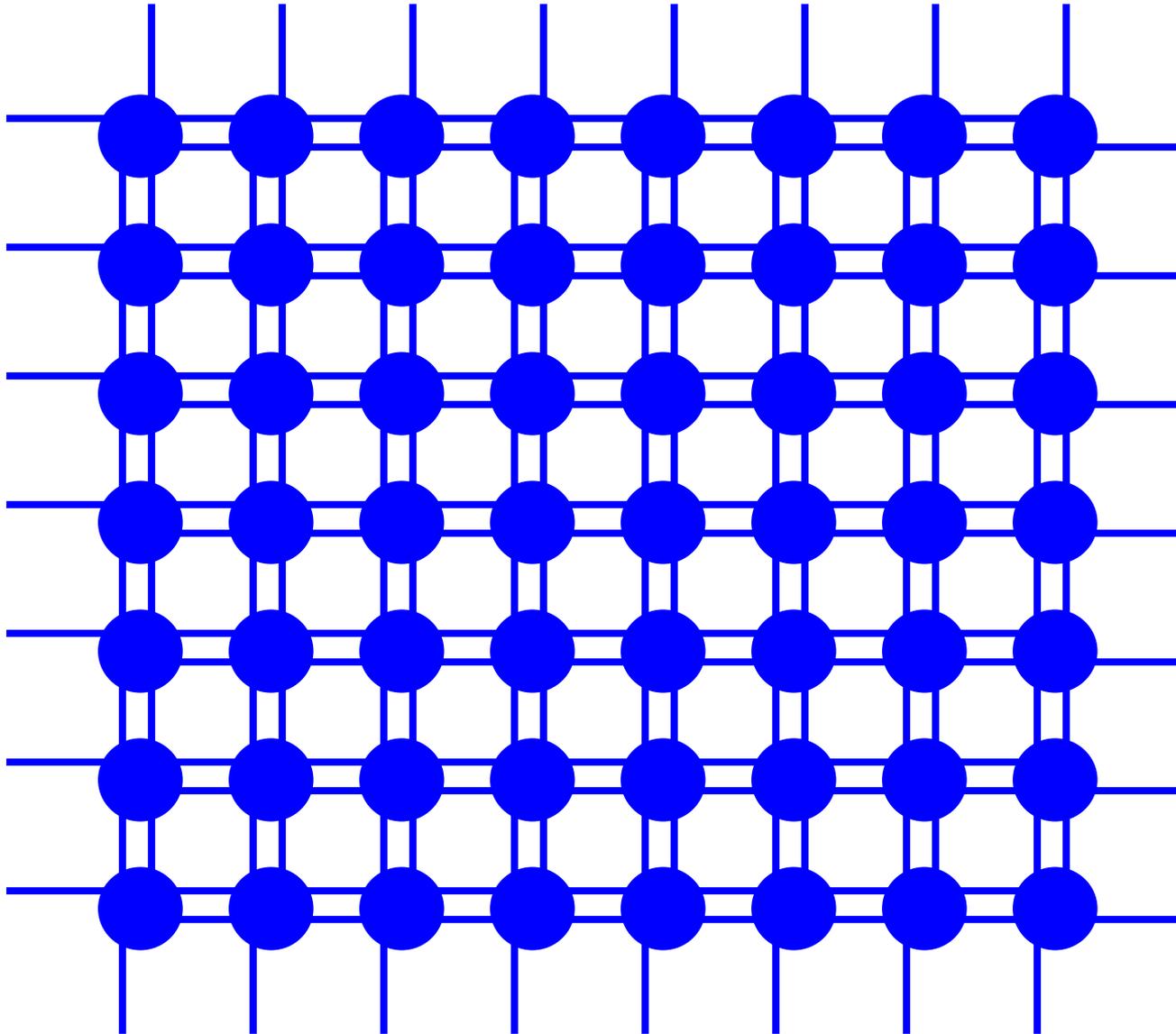






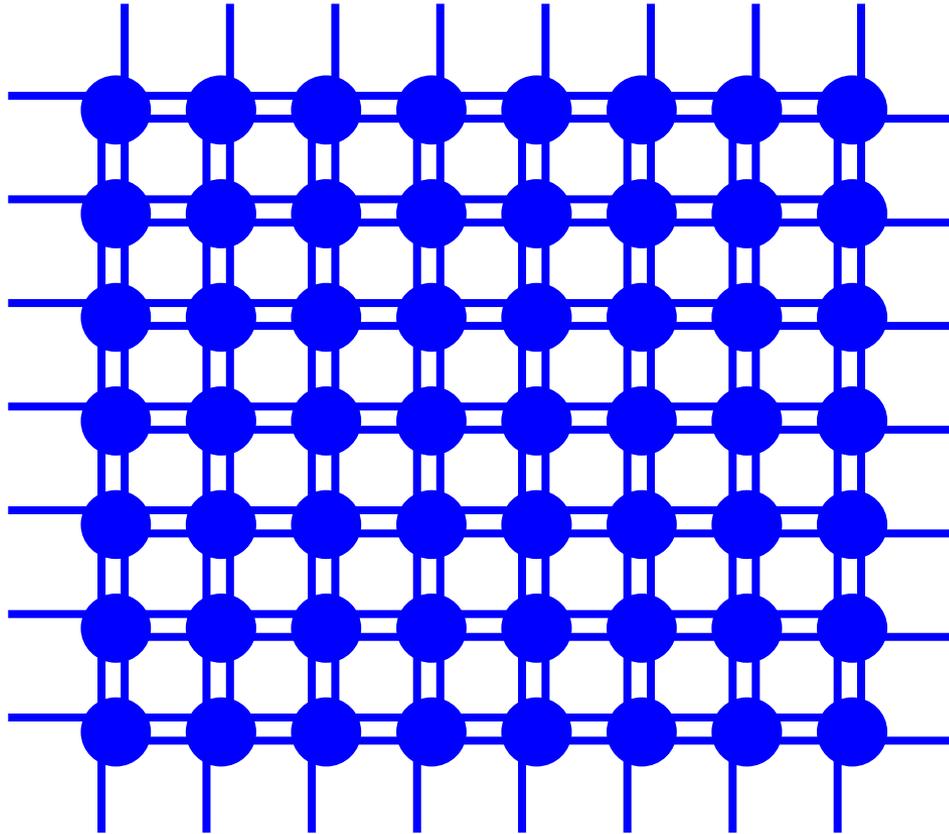






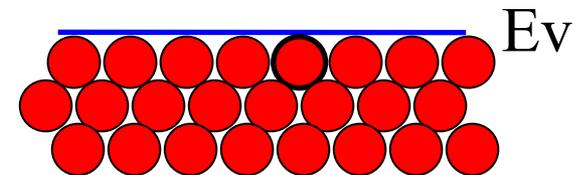
# Band Occupation at Low Temperature (0 Kelvin)

For  $(E_{\text{thermal}}=kT)=0$



No electrons in conduction band means no electron conduction is possible

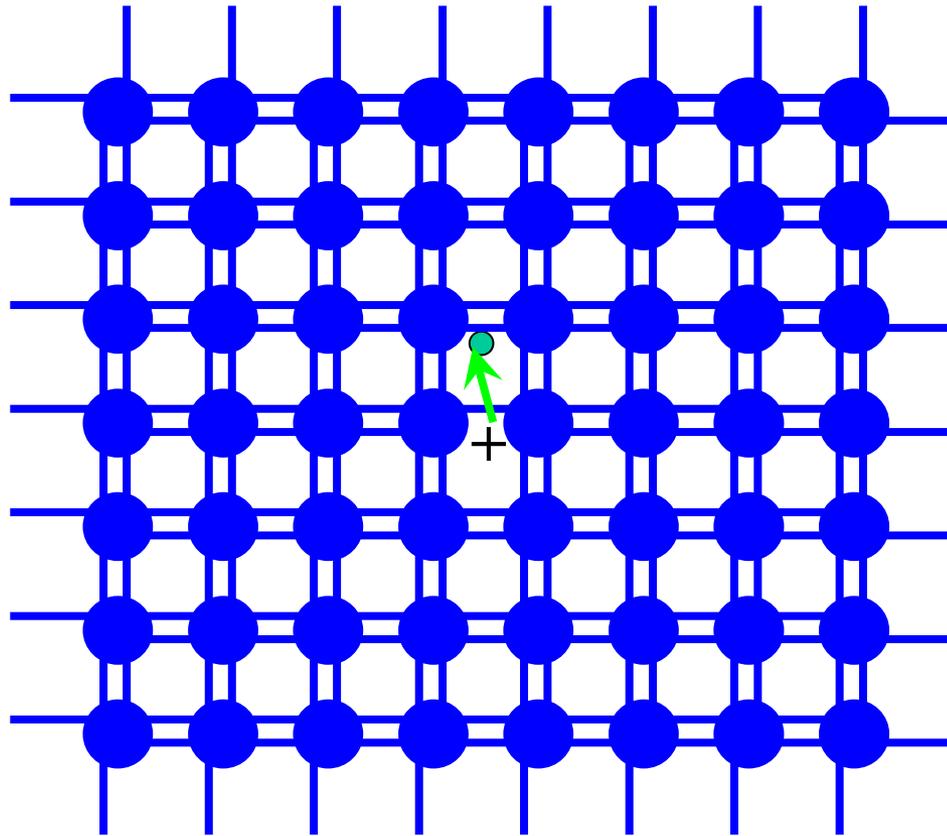
—————  $E_c$



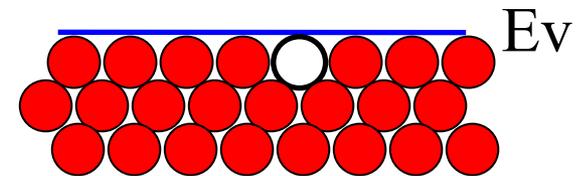
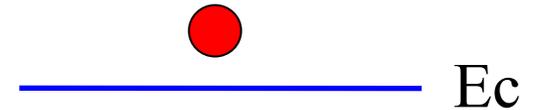
No “Holes” valence band means no “hole” conduction is possible

# Band Occupation at Higher Temperature ( $T > 0$ Kelvin)

For  $(E_{\text{thermal}} = kT) > 0$



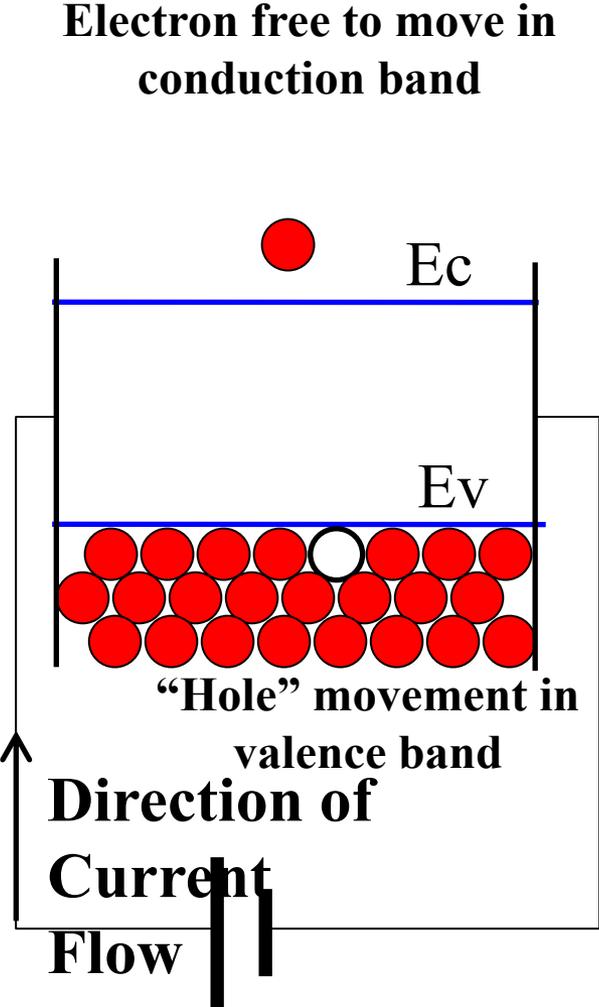
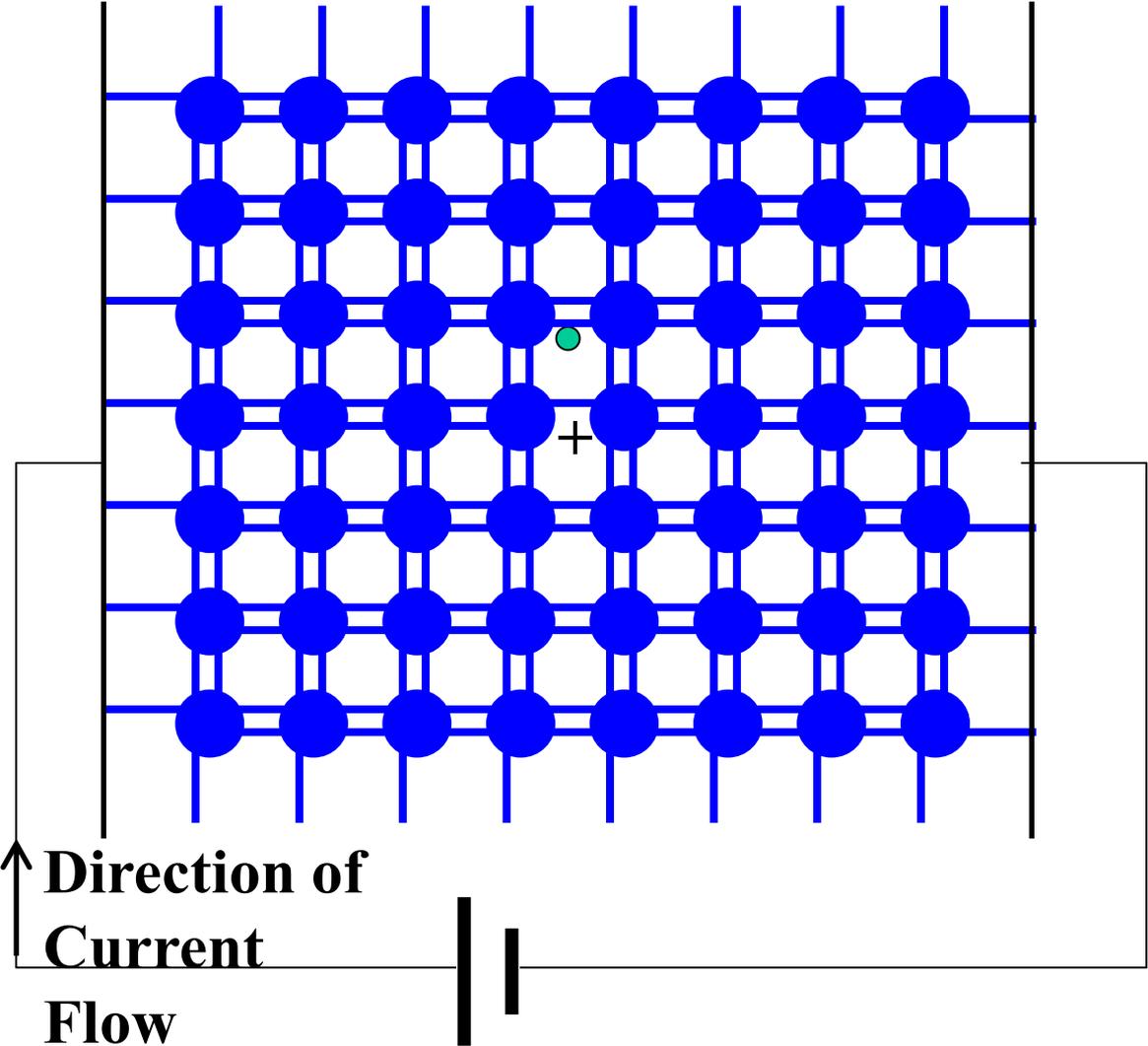
Electron free to move  
in conduction band



“Hole” free to move in  
valence band

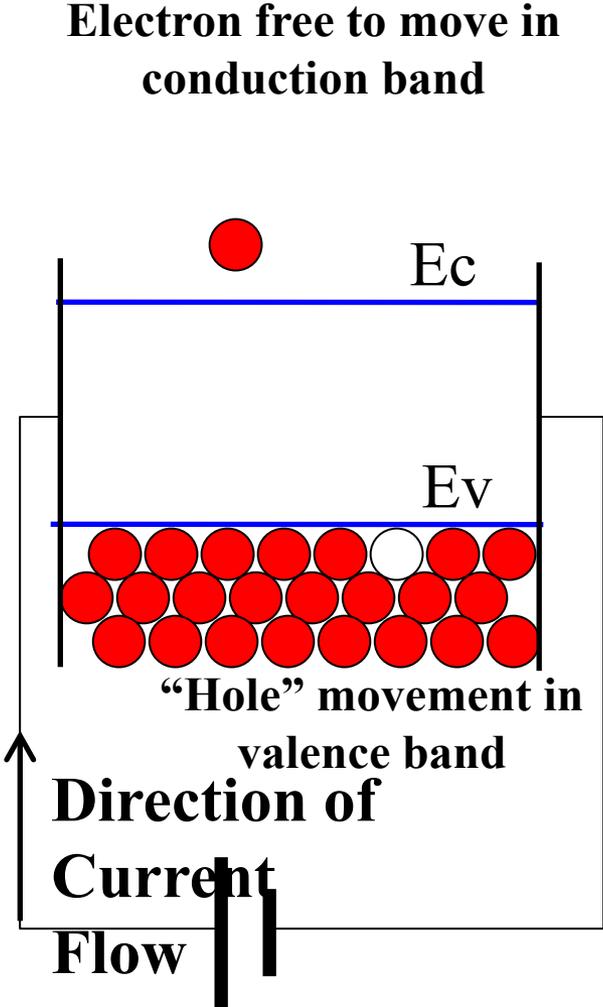
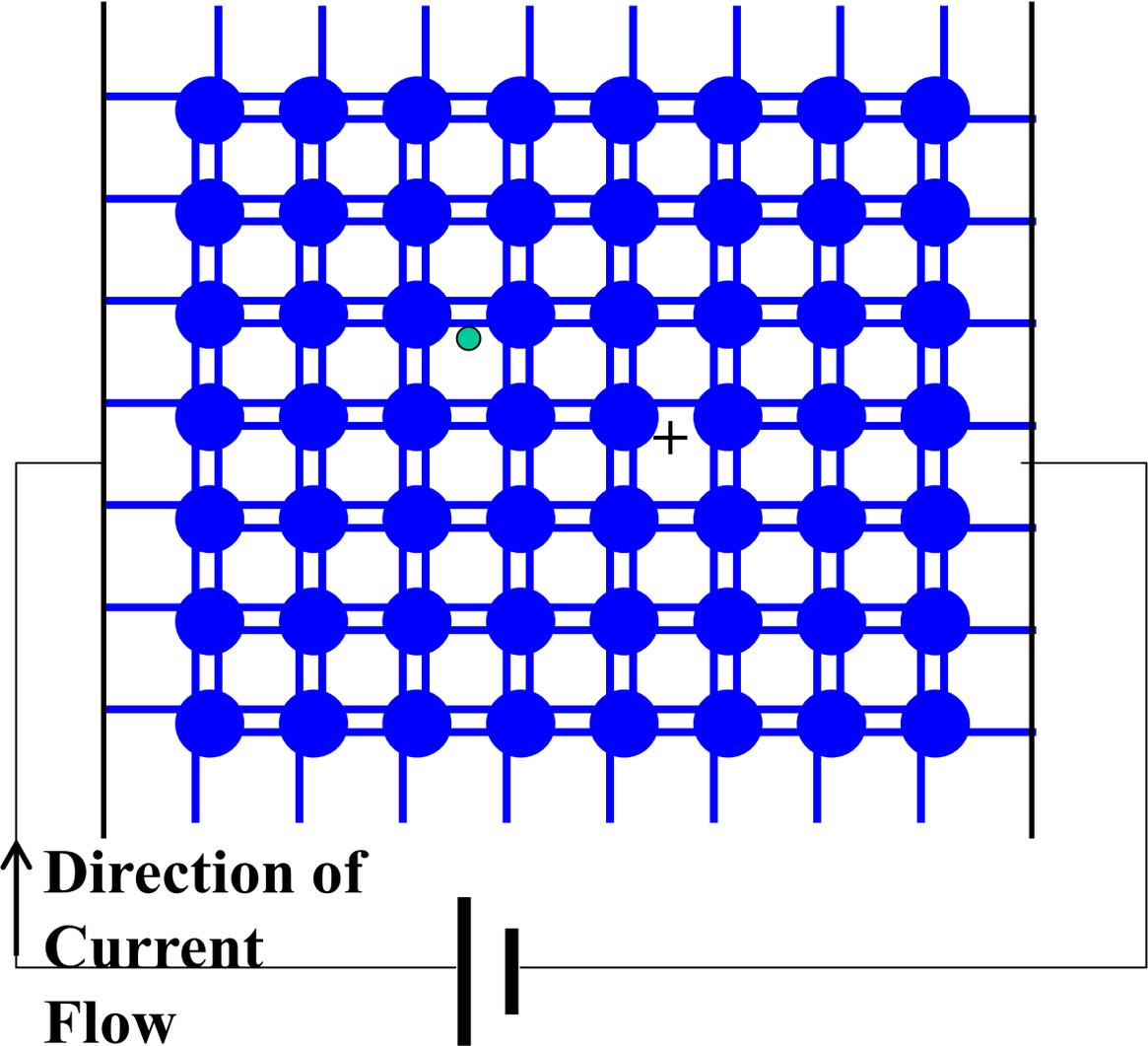
# Carrier Movement Under Bias

For  $(E_{\text{thermal}} = kT) > 0$



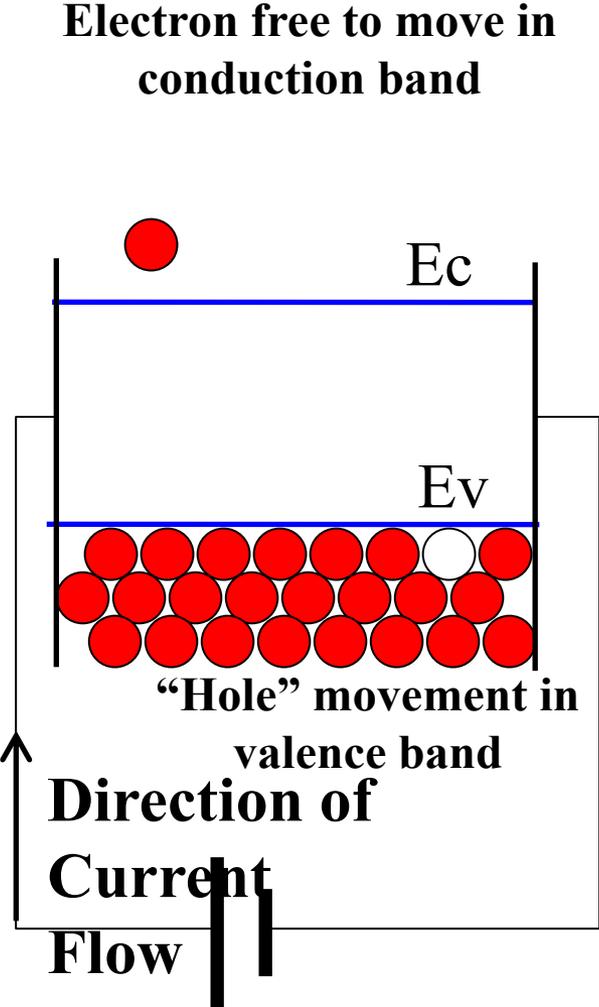
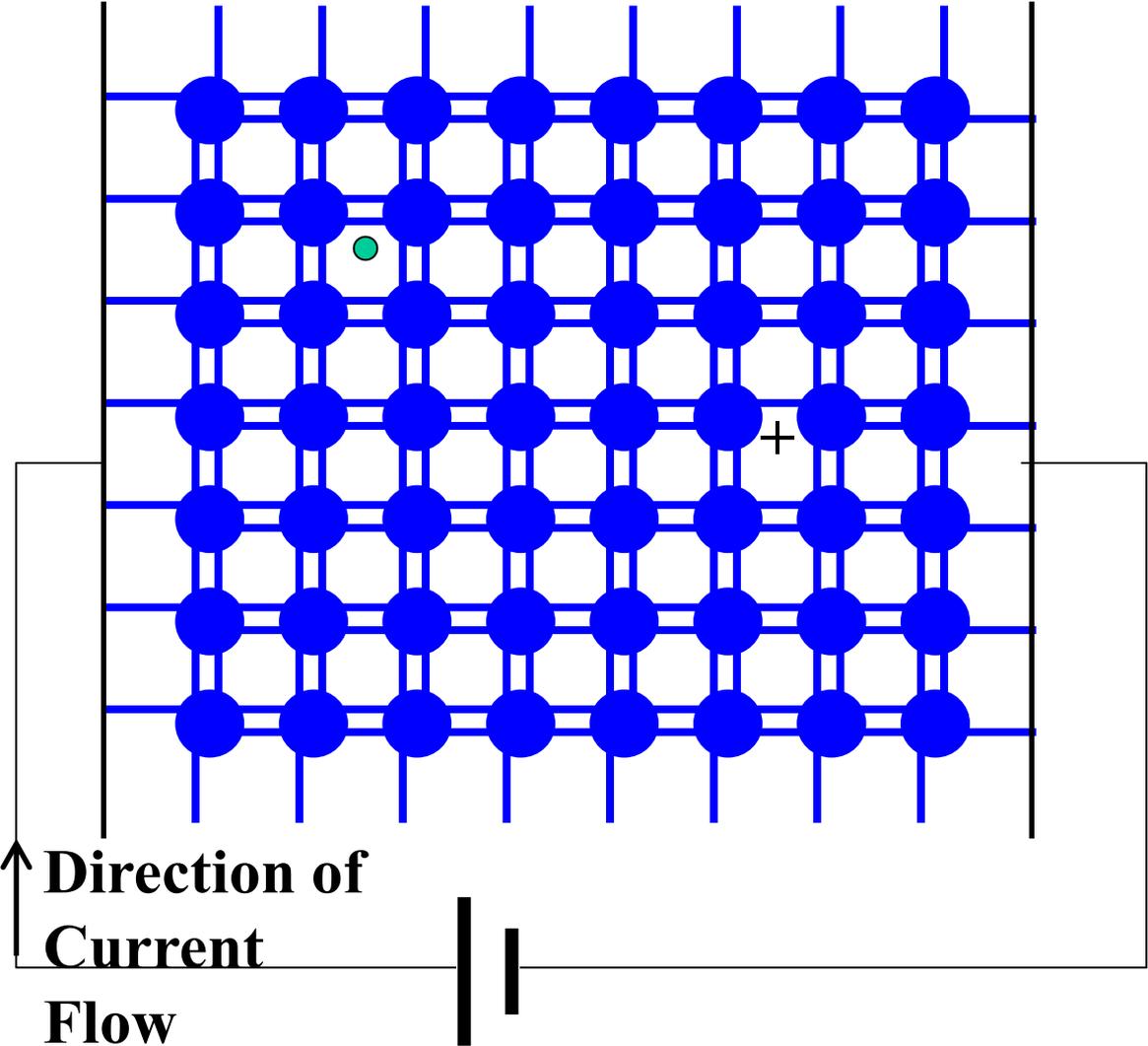
# Carrier Movement Under Bias

For  $(E_{\text{thermal}} = kT) > 0$



# Carrier Movement Under Bias

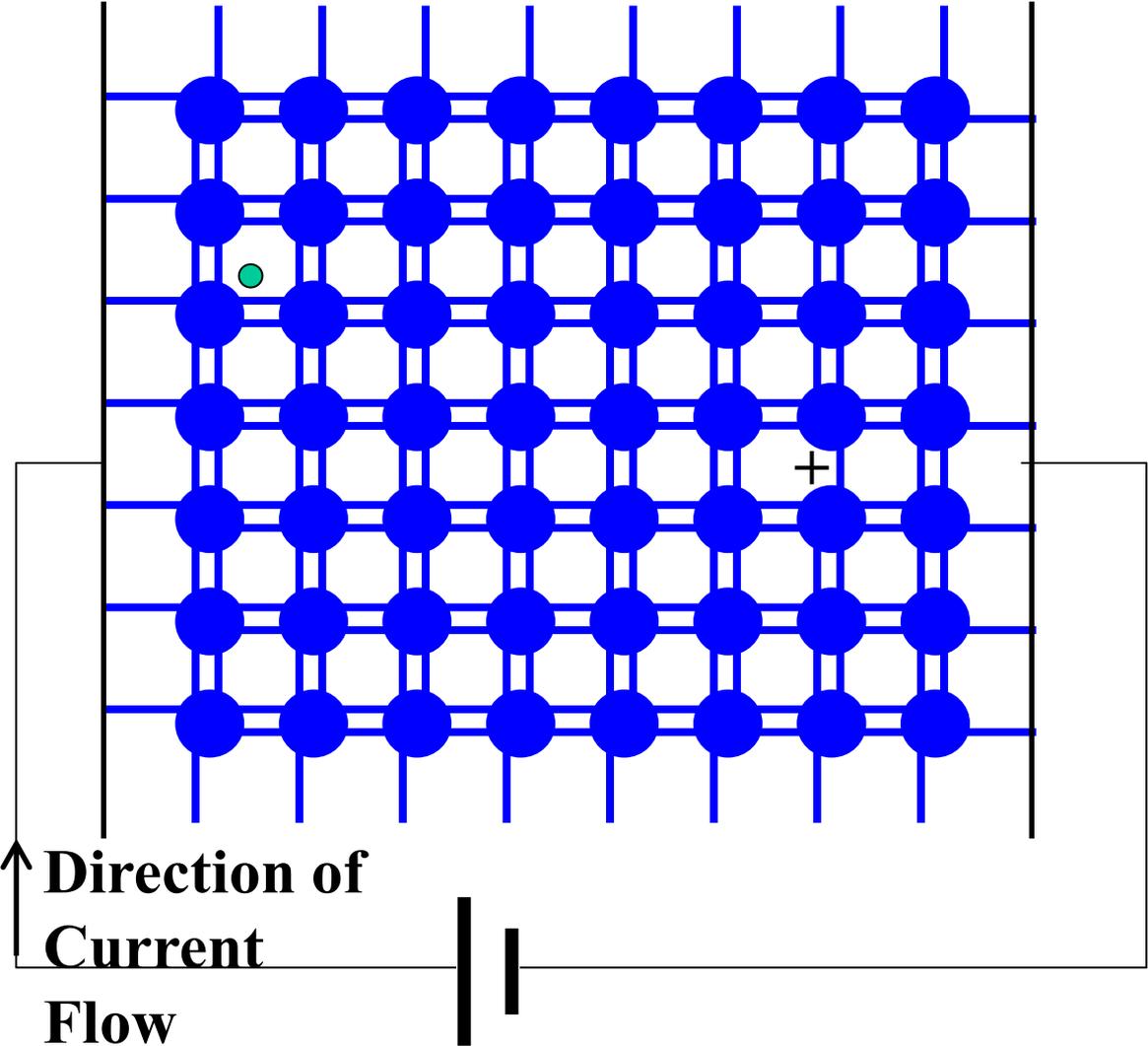
For  $(E_{\text{thermal}} = kT) > 0$



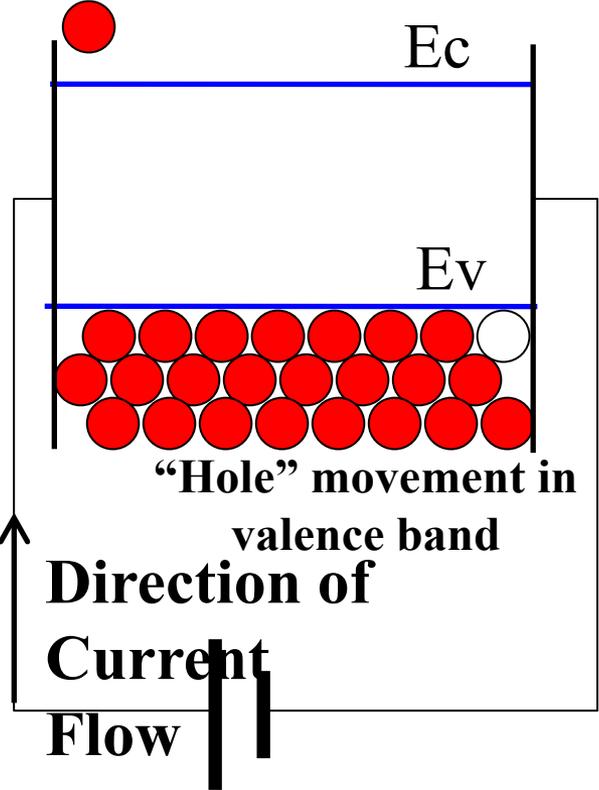
# Carrier Movement Under Bias



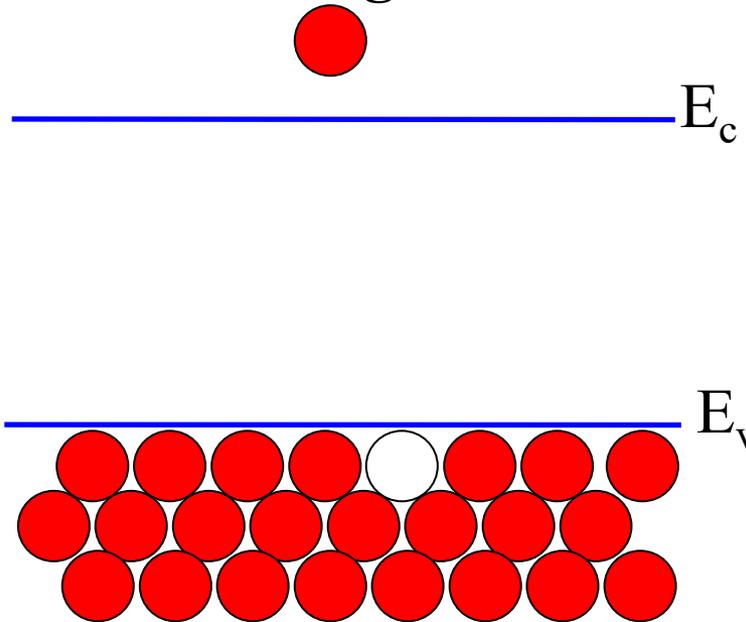
For  $(E_{\text{thermal}} = kT) > 0$



Electron free to move in conduction band



# Clarification of confusing issues: “Holes” and Electrons



The valence band may have  $\sim 4e22 \text{ cm}^{-3}$  valence electrons “participating in the bonding processes holding the crystal together.

The valence band might only have  $\sim 1e6$  to  $1e19 \text{ cm}^{-3}$  “holes” in the valence band (missing valence electrons). Thus, it is easier to account for the influence of the holes by counting the holes directly as apposed to counting very small changes in the valence electron concentrations.

**Example:** If there are  $1e22 \text{ cm}^{-3}$  atoms in a crystal with each atom having 4 valence electrons. What is the difference in valence electron concentration for  $1e12$  holes verses  $1e13 \text{ cm}^{-3}$  holes?

$$\text{Answer: } 4 \times 1e22 \text{ cm}^{-3} - 1e12 \text{ cm}^{-3} = 3.9999999999e22 \text{ cm}^{-3} \text{ verses}$$

$$4 \times 1e22 \text{ cm}^{-3} - 1e13 \text{ cm}^{-3} = 3.999999999e22 \text{ cm}^{-3}$$

**For “accounting reasons” keeping track of holes is easier!**

# Clarification of confusing issues: “Holes” and Electrons

## Terminology

Only these “particles” carry electric *ity*. Thus, we call these “carriers”

Electrons: Sometimes referred to as conduction electrons: The electrons in the conduction band that are free to move throughout the crystal.

Holes: Missing electrons normally found in the valence band (or empty states in the valence band that would normally be filled).

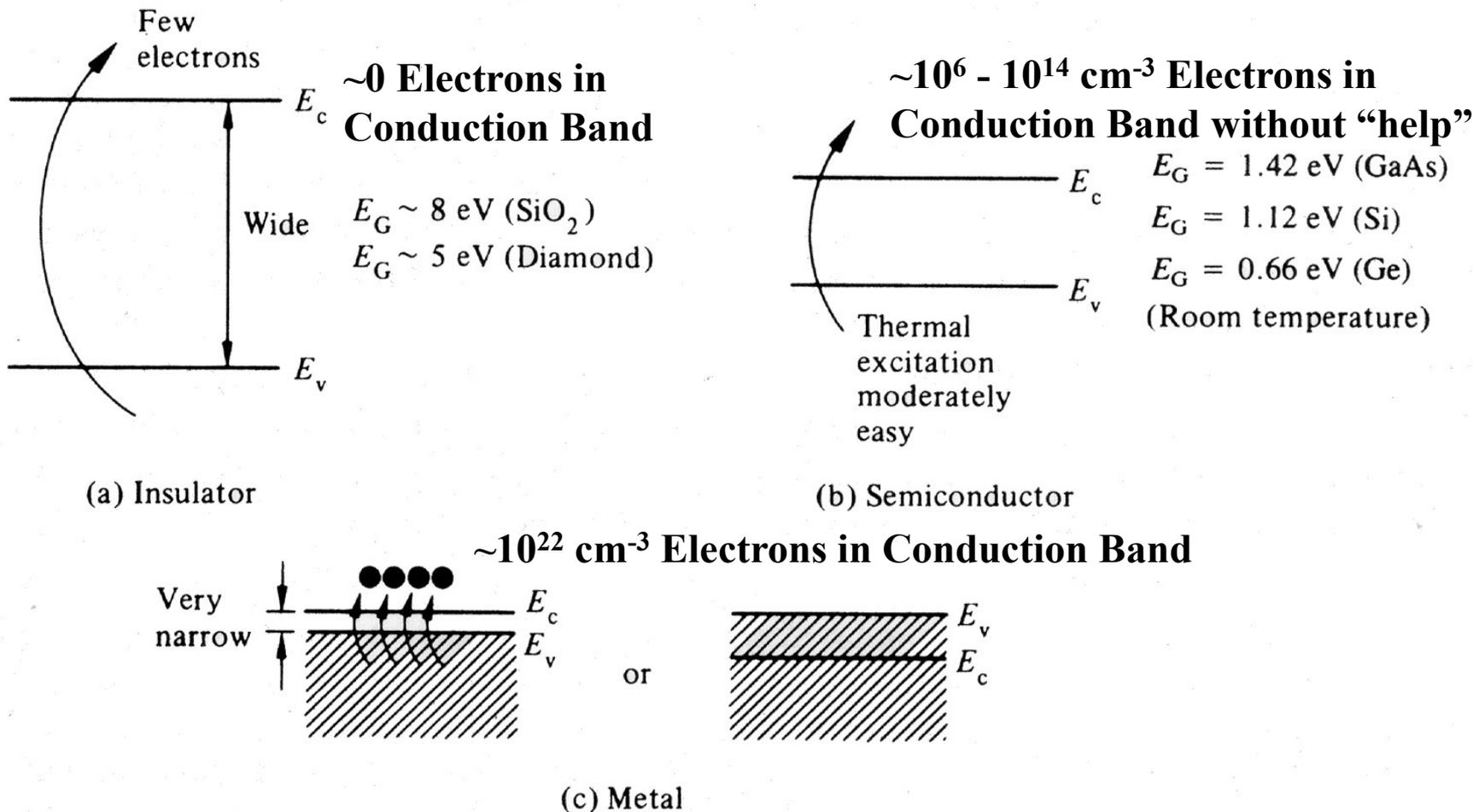
If we talk about empty states in the conduction band, we DO NOT call them holes! This would be confusing. The conduction band has mostly empty states and a few electrons.

If we talk about filled states in the valence band, we DO NOT call them electrons! This would be confusing. We can call them Valence Electrons to indicate they are bond to atoms (in the valence shells of atoms). The valence band has mostly filled states and a few holes.

For the vast majority of this class we only talk about electrons (conduction band electrons) and holes (empty states in the valence band)!

# Material Classification based on Size of Bandgap:

Ease of achieving thermal population of conduction band determines whether a material is an insulator, semiconductor, or metal



**Figure 2.8** Explanation of the distinction between (a) insulators, (b) semiconductors, and (c) metals using the energy band model.

# Intrinsic Carrier Concentration

- For each electron promoted to the conduction band, one hole is left in the valence band. Thus, the number of electrons in the conduction band is equal to the number of holes in the valence band unless there is “help” to change the relative populations in each band.
- Intrinsic carrier concentration is the number of electron (=holes) per cubic centimeter populating the conduction band (or valence band) is called the intrinsic carrier concentration,  $n_i$
- $n_i = f(T)$  that increases with increasing  $T$  (more thermal energy)

## At Room Temperature ( $T=300$ K)

$n_i \sim 2 \times 10^6 \text{ cm}^{-3}$  for GaAs with  $E_g = 1.42 \text{ eV}$ ,

$n_i \sim 1 \times 10^{10} \text{ cm}^{-3}$  for Si with  $E_g = 1.1 \text{ eV}$ ,

$n_i \sim 2 \times 10^{13} \text{ cm}^{-3}$  for Ge with  $E_g = 0.66 \text{ eV}$ ,

$n_i \sim 1 \times 10^{-14} \text{ cm}^{-3}$  for GaN with  $E_g = 3.4 \text{ eV}$

# **Dopants**

**Reading:  
(Cont'd) Notes**

# The need for more control over carrier concentration

Without “help” the total number of “carriers” (electrons and holes) is limited to  $2n_i$ .

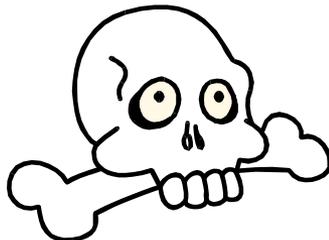
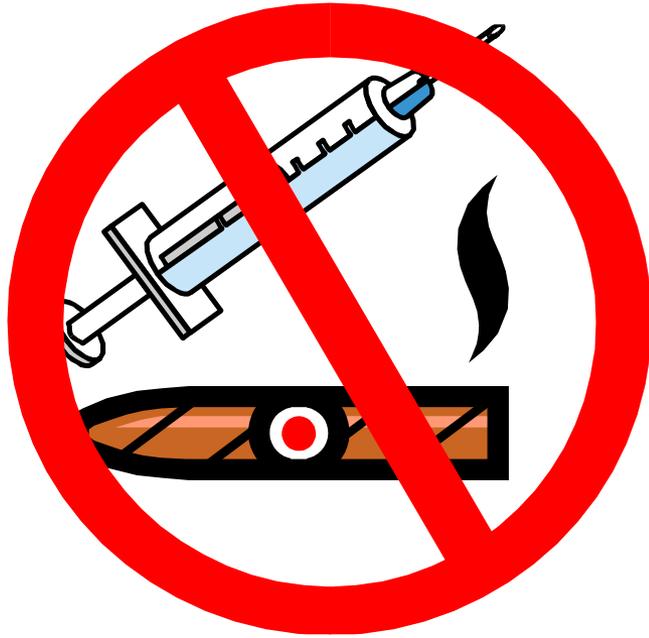
For most materials, this is not that much, and leads to very high resistance and few useful applications.

We need to add carriers by modifying the crystal.

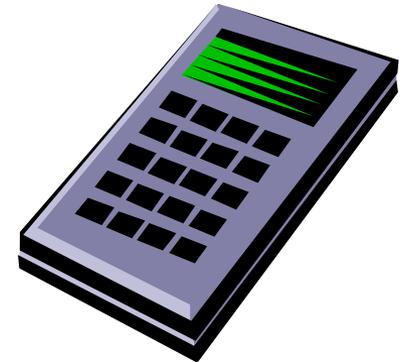
This process is known as “doping the crystal”.

# Regarding Doping, ...

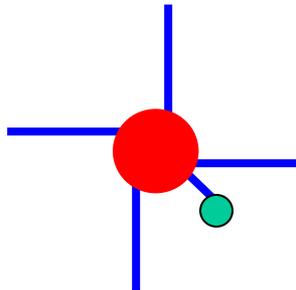
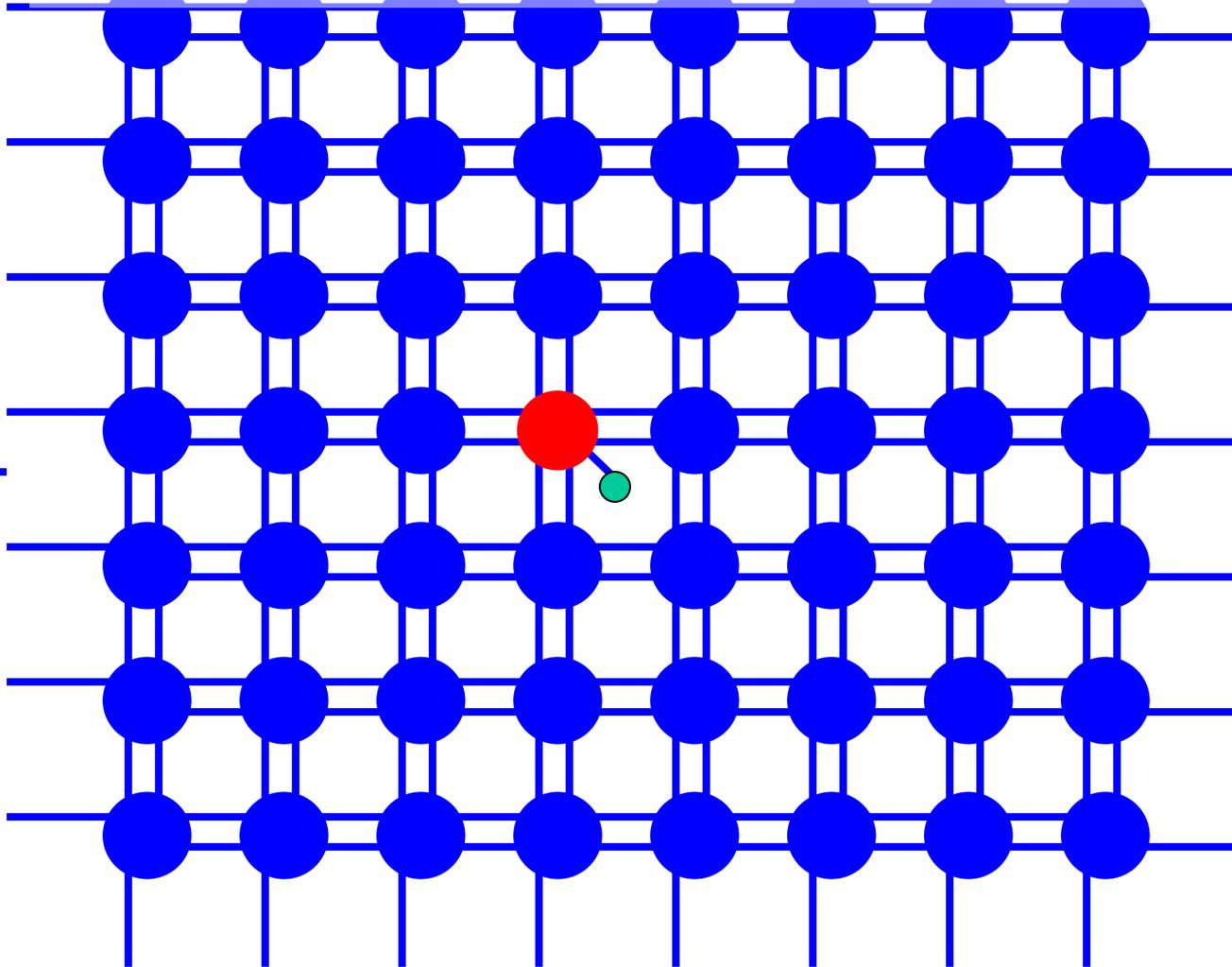
**Just Say No!**



**Just Say Yes  
to Crystal Doping!**



# Extrinsic, (or doped material): Concept of a Donor “adding extra” electrons



**Example:**  
P, As, Sb  
in Si

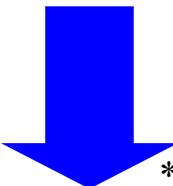
# Concept of a Donor “adding extra” electrons

Use the Hydrogen Atomic Energy levels to approximate the energy required to free an electron on a donor.

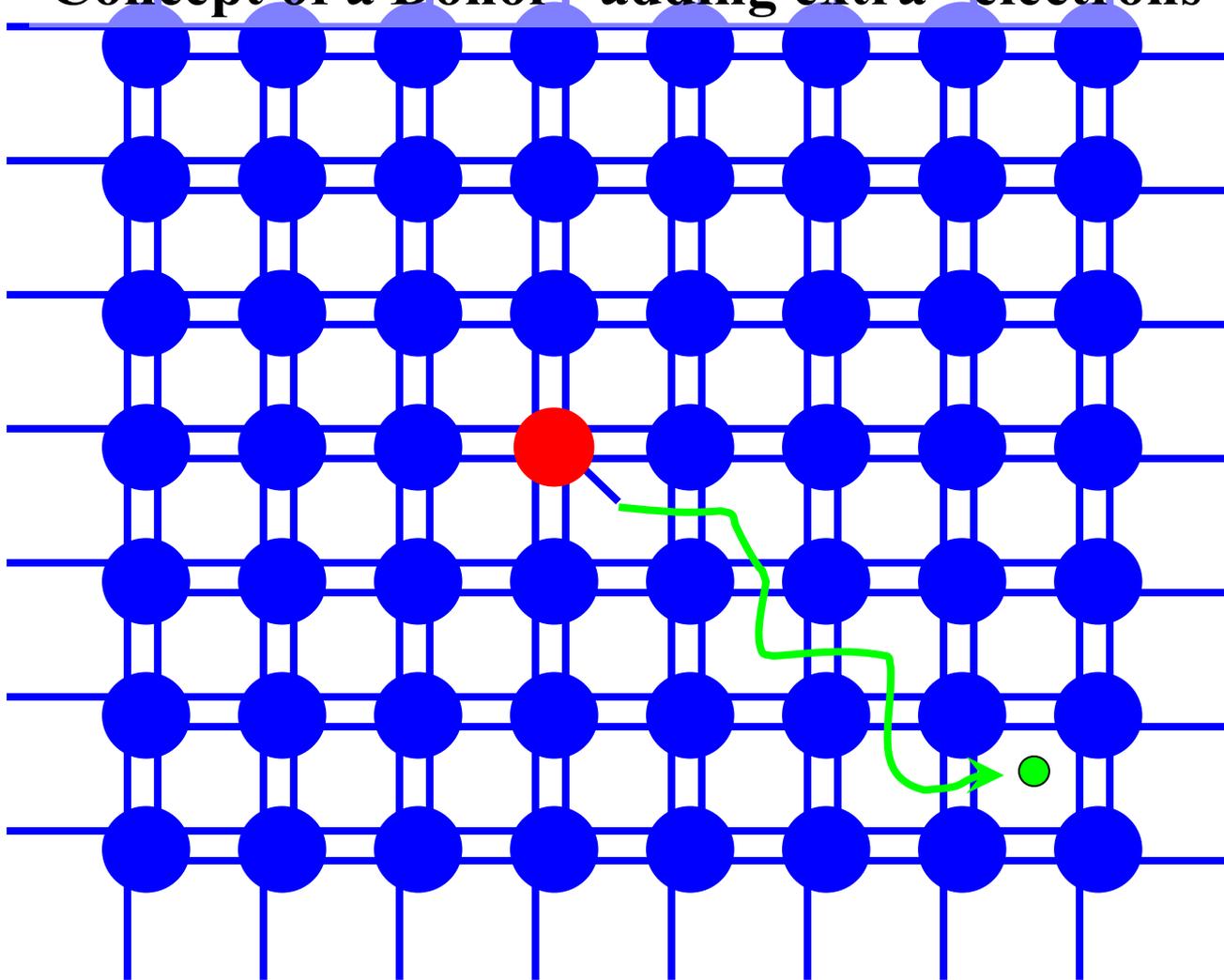
- Replace dielectric constant with that of the semiconductor
- Replace mass with that of the semiconductor

$$\text{Energy}_{\text{Hydrogen electron}} = E_H = -\frac{m_o q^4}{2(4\pi\epsilon_o \hbar n)^2} = -\frac{13.6 \text{ eV}}{n^2}$$

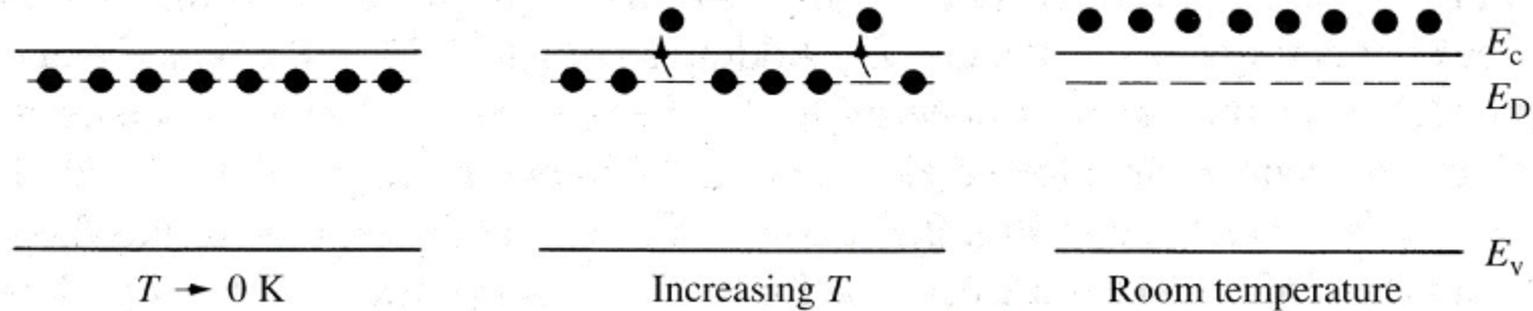
where  $m_o$  = electron mass,  $\hbar = \text{planks constant} / 2\pi = h / 2\pi$   
 $q = \text{electron charge}$ , and  $n = 1, 2, 3, \dots$


$$E_{\text{Binding for electron}} \approx -\frac{m_n^* q^4}{2(4\pi\epsilon_R \epsilon_o \hbar n)^2} = \frac{m_n^*}{m_o} \frac{1}{\epsilon_R^2} E_H \cong -0.1 \text{ eV for } n = 1$$

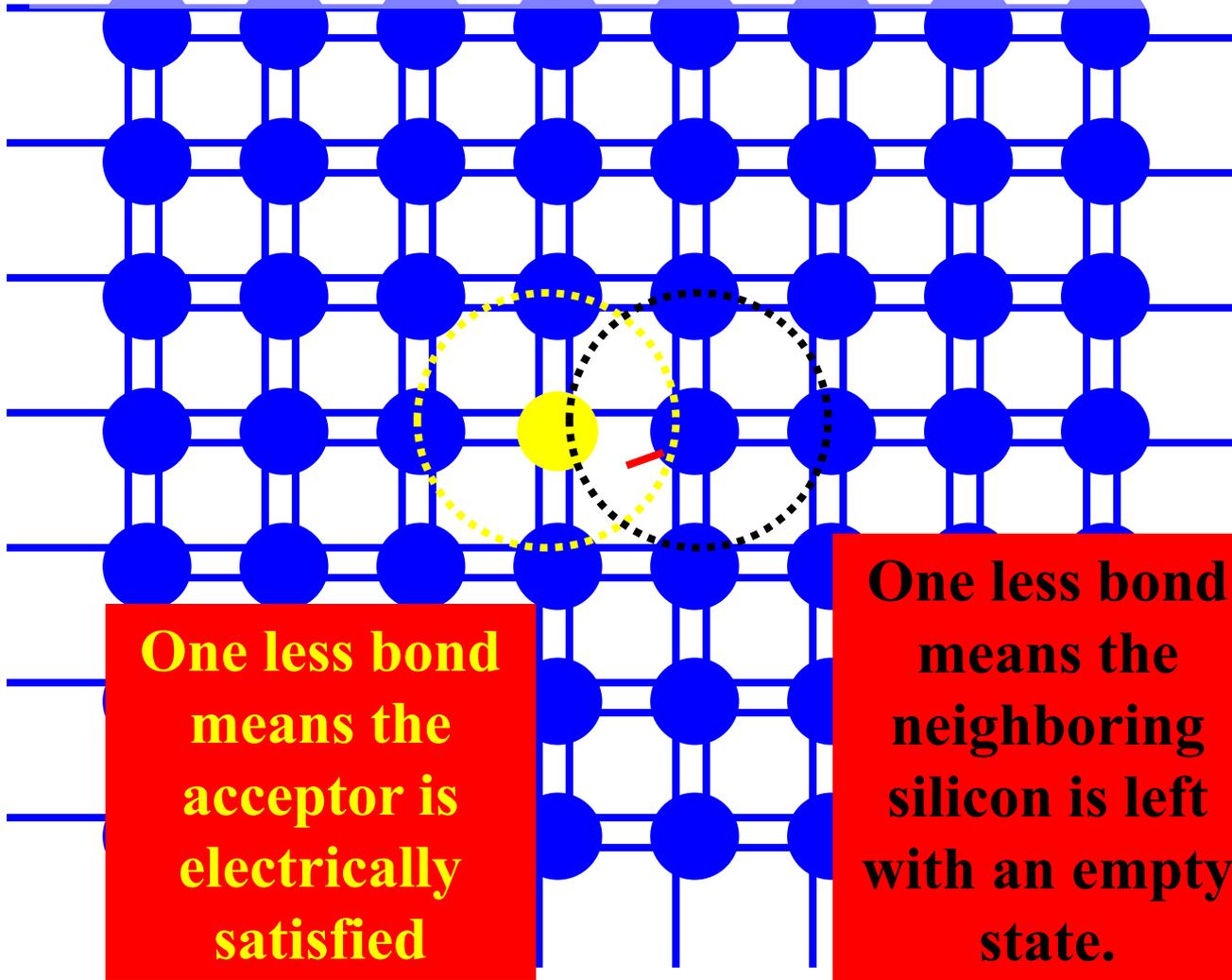
**Extrinsic, (or doped material):  
Concept of a Donor “adding extra” electrons**



# Concept of a Donor “adding extra” electrons: Band diagram equivalent view



# Extrinsic, (or doped material): Concept of an acceptor “adding extra” holes



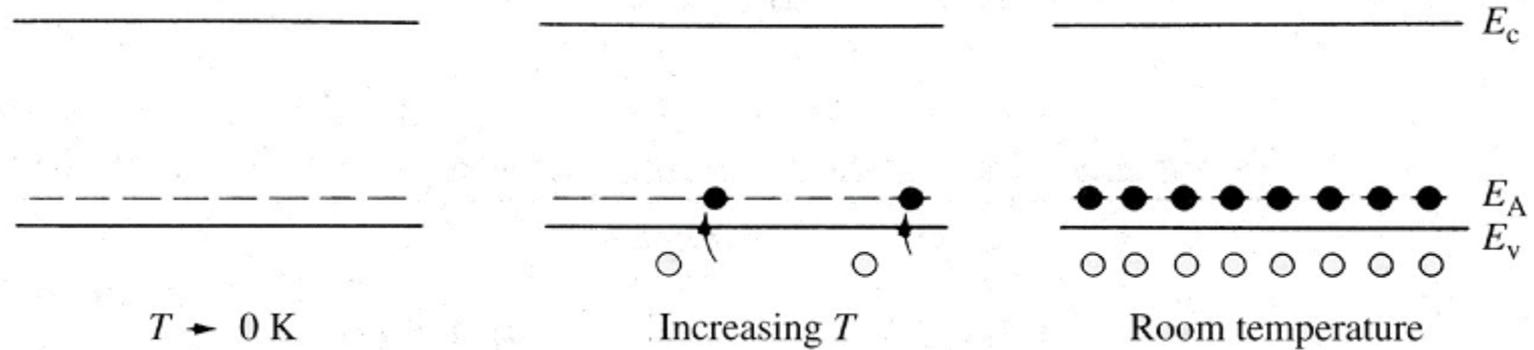
All regions of material are neutrally charged.

**One less bond means the acceptor is electrically satisfied**

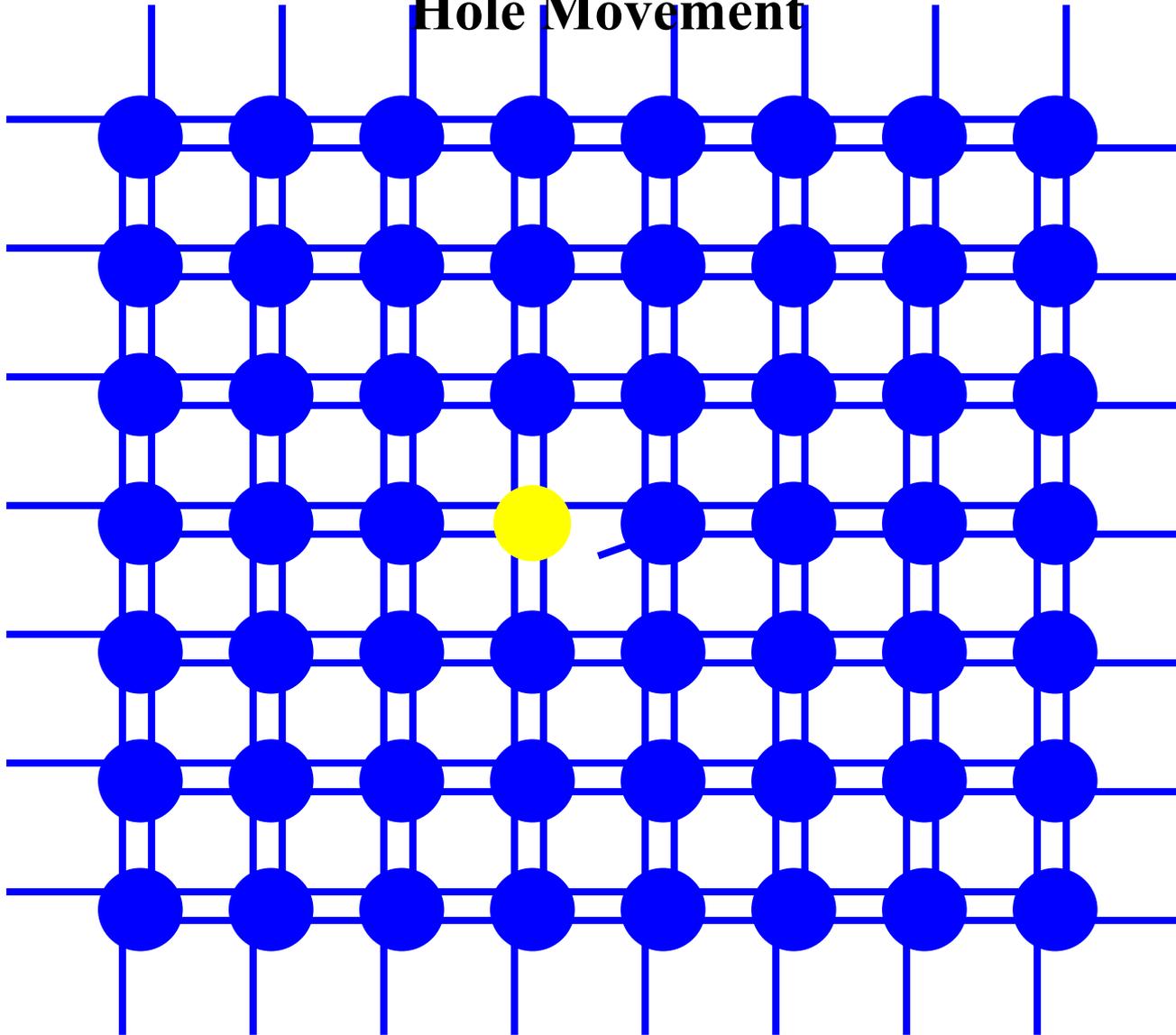
**One less bond means the neighboring silicon is left with an empty state.**

**Example:  
B, Al, In  
in Si**

# Concept of an Acceptor “adding extra hole”: Band diagram equivalent view



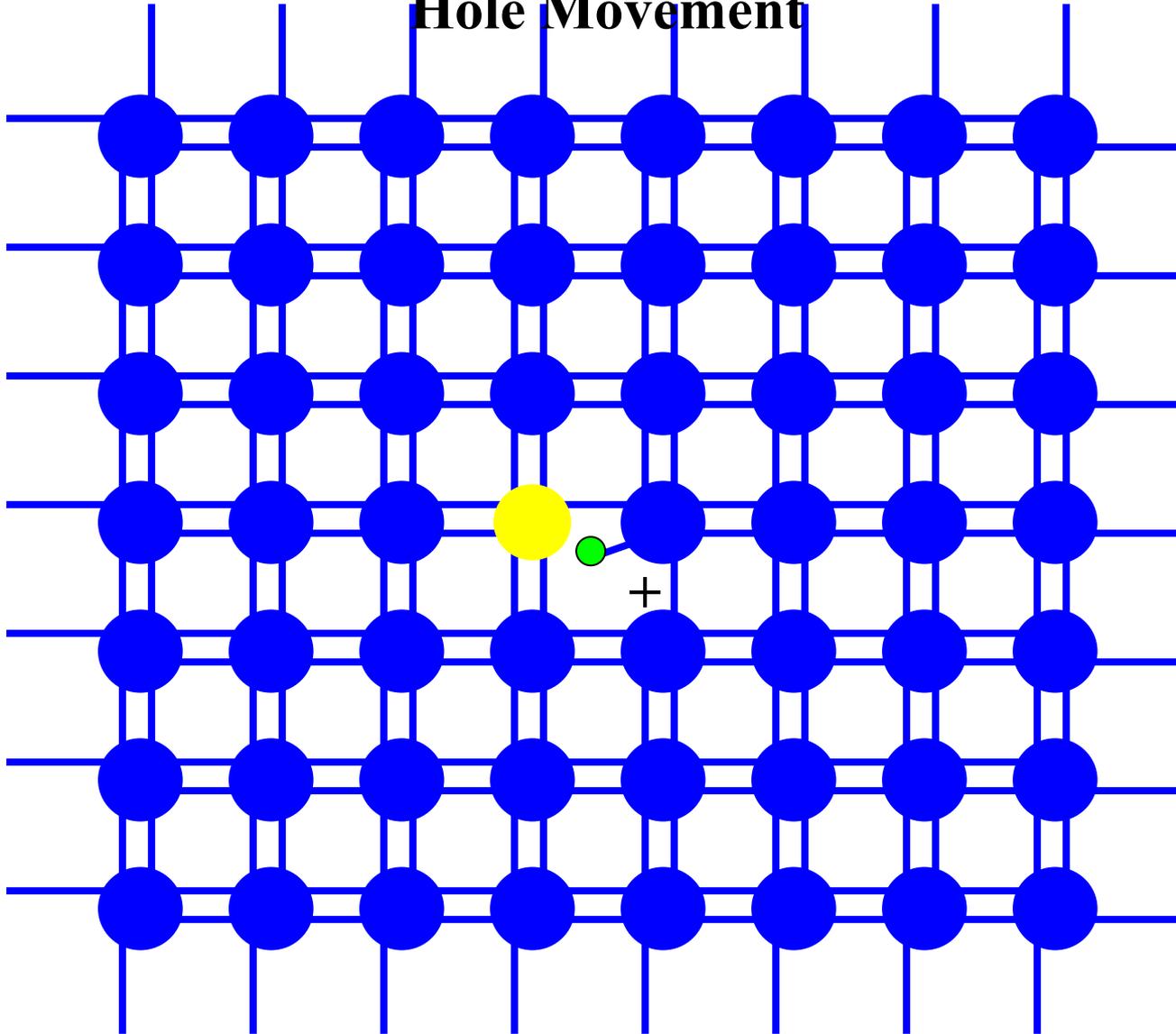
# Hole Movement



All regions of material are neutrally charged.

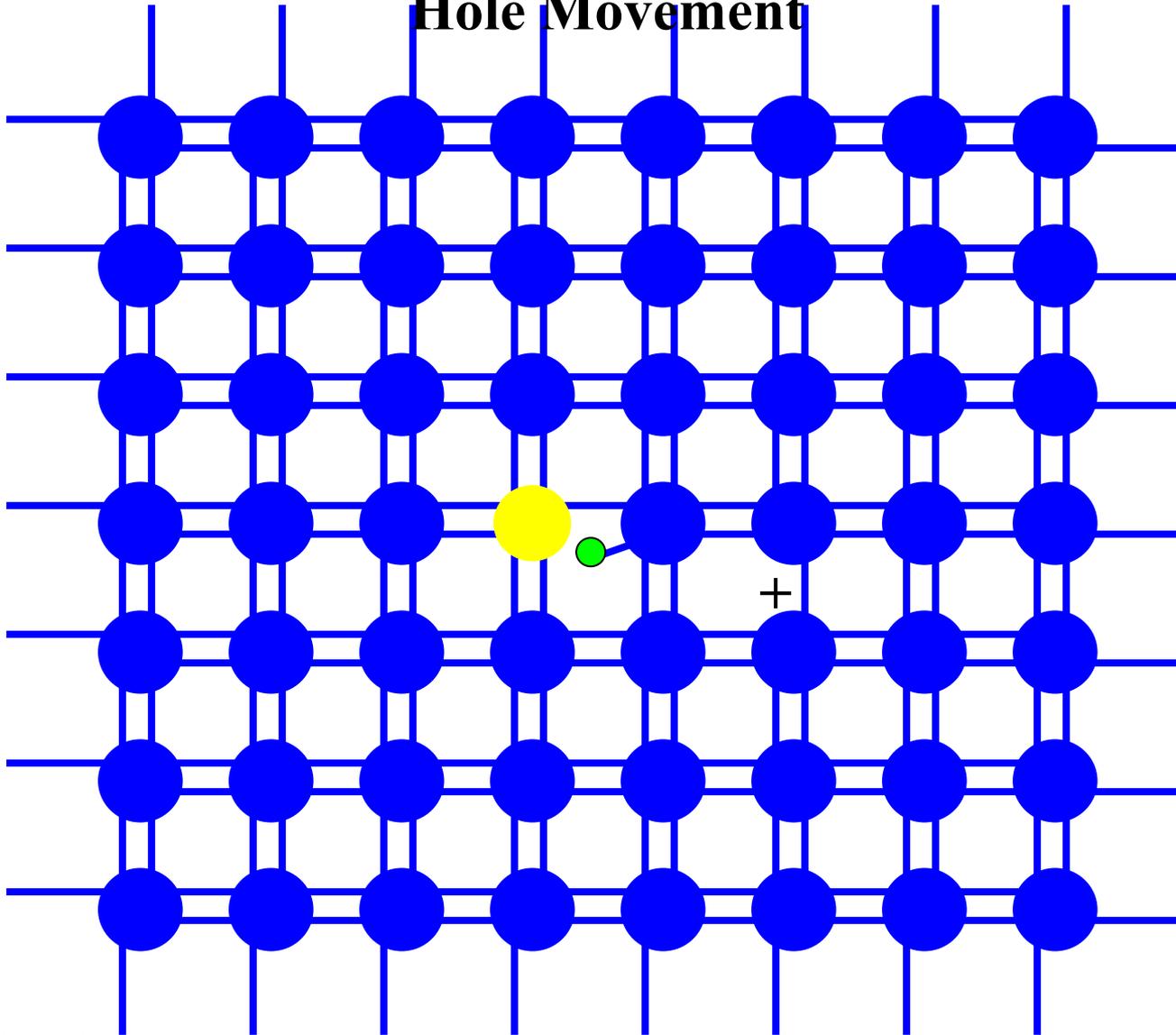
Empty state is located next to the Acceptor

## Hole Movement



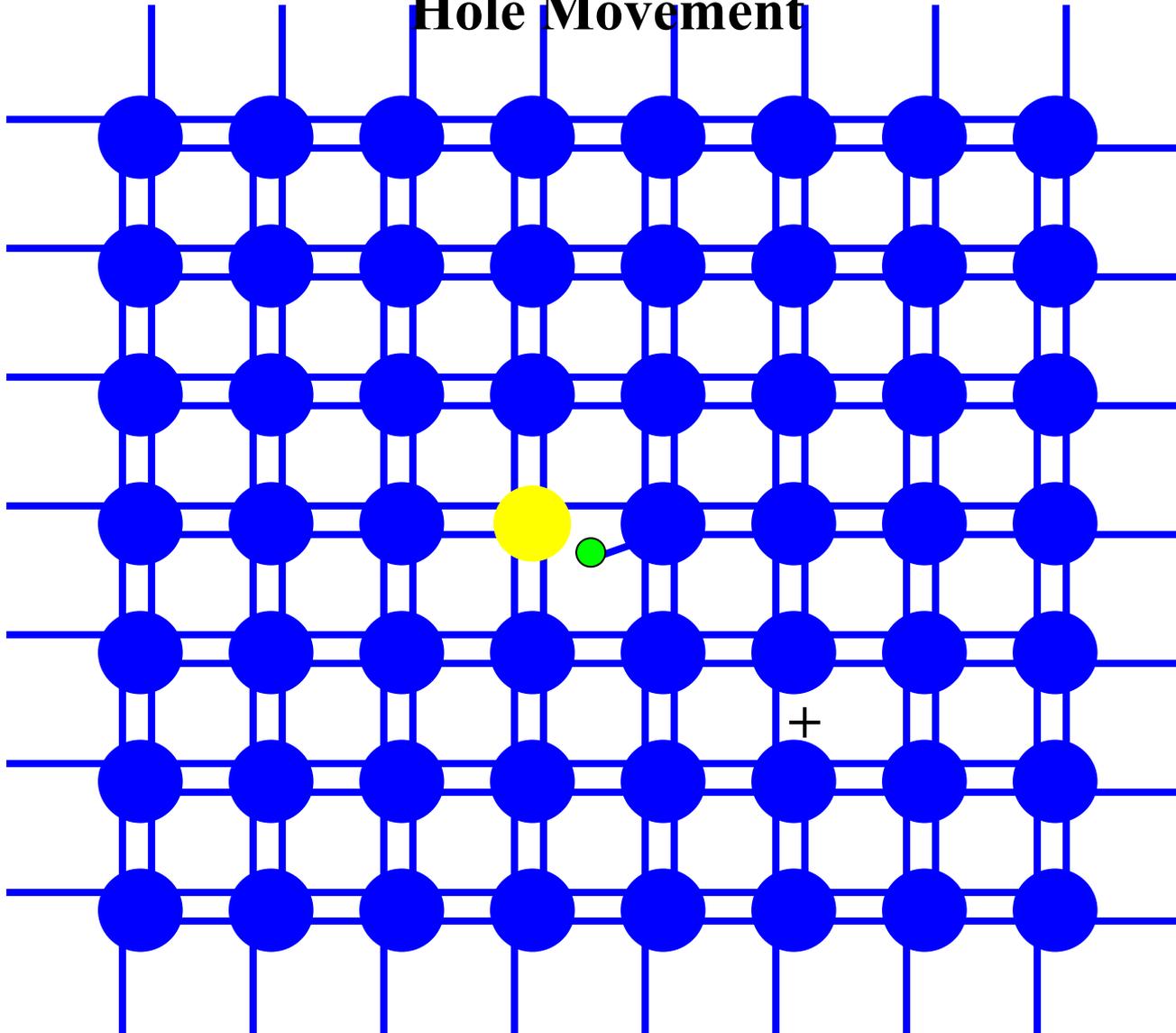
Another valence electron can fill the empty state located next to the Acceptor leaving behind a positively charged “hole”.

## Hole Movement



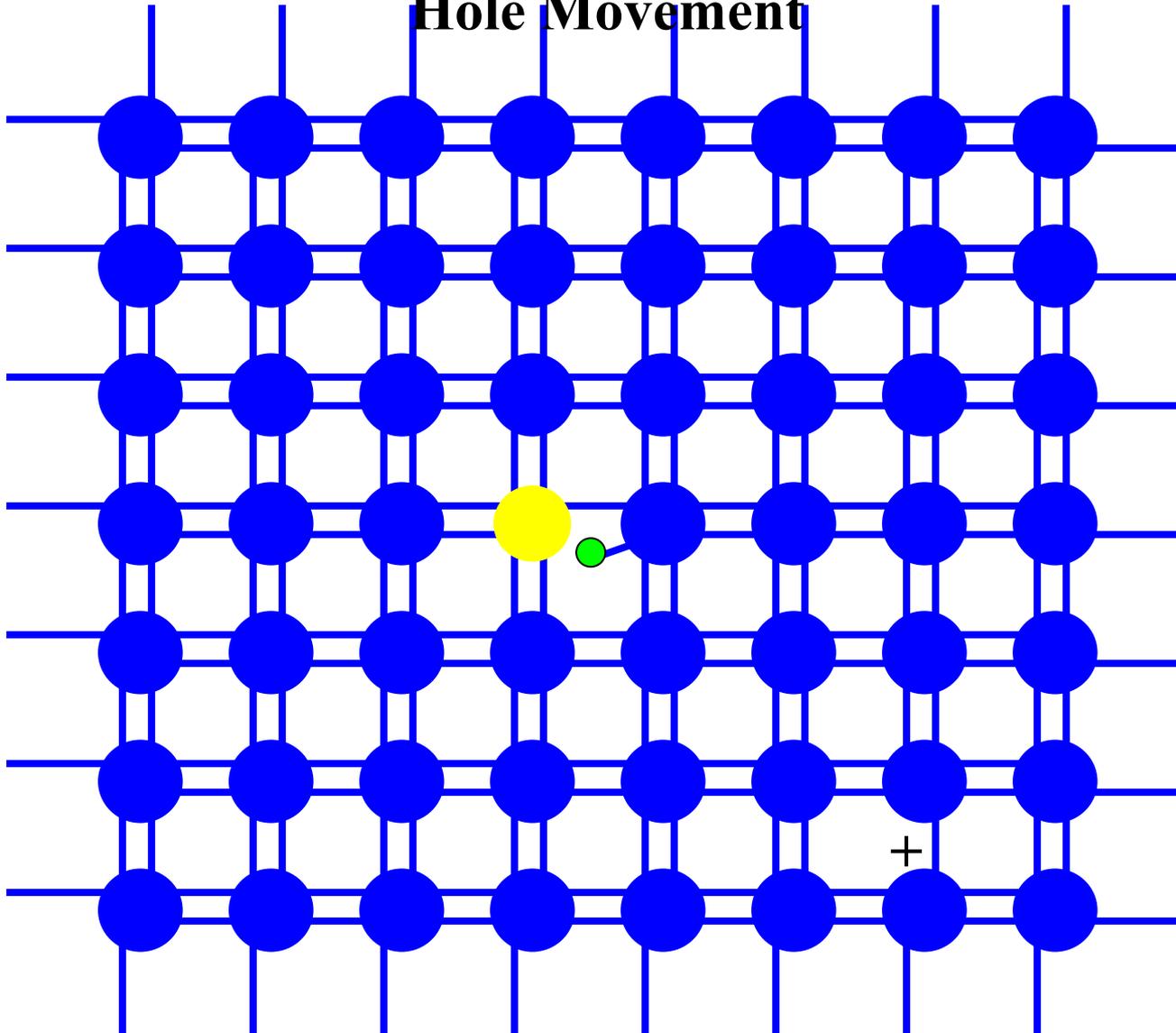
The positively charged “hole” can move throughout the crystal (really it is the valance electrons jumping from atom to atom that creates the hole motion).

## Hole Movement



The positively charged “hole” can move throughout the crystal (really it is the valance electrons jumping from atom to atom that creates the hole motion).

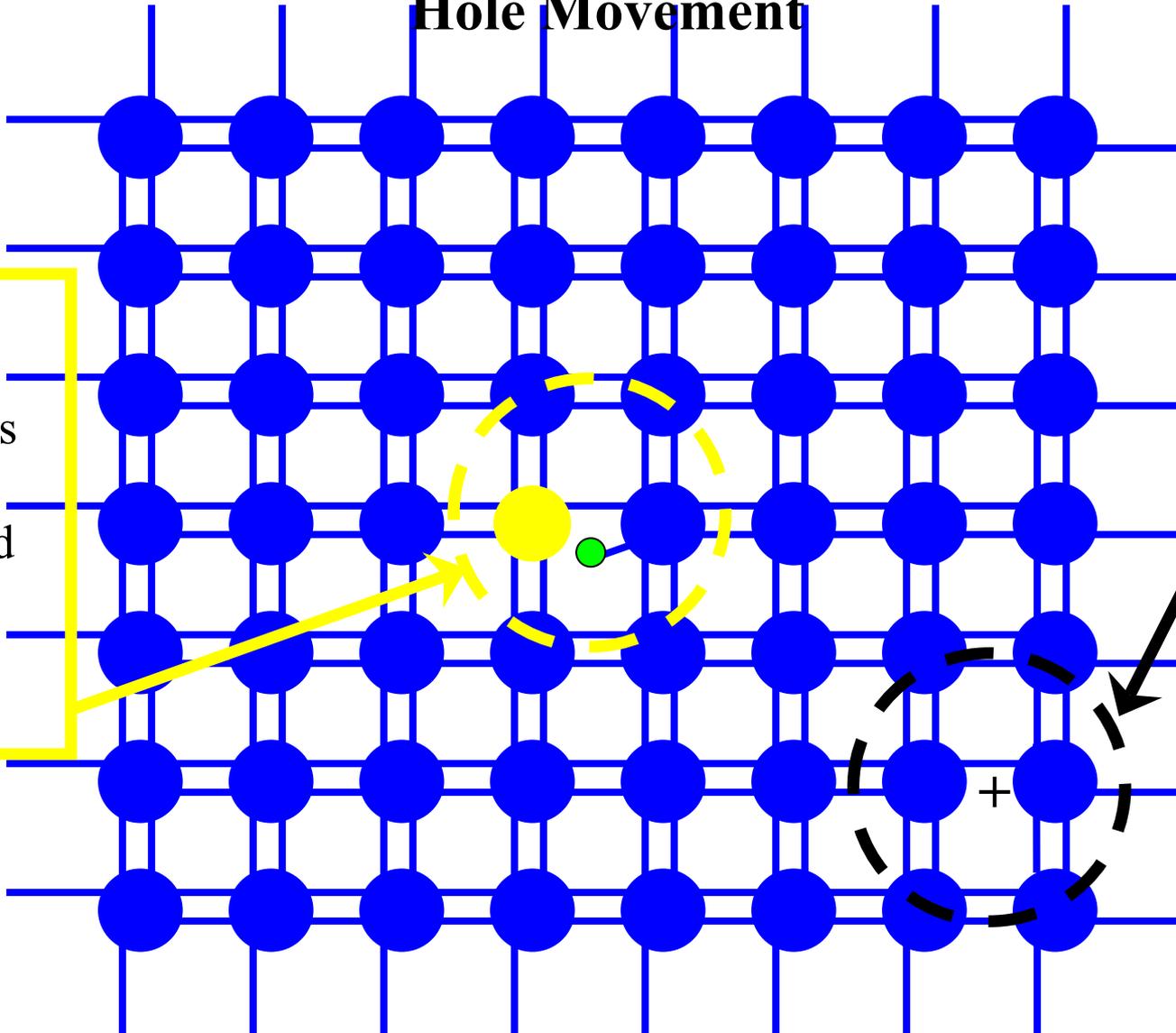
## Hole Movement



The positively charged “hole” can move throughout the crystal (really it is the valance electrons jumping from atom to atom that creates the hole motion).

# Hole Movement

Region around the acceptor has one extra electron and thus is negatively charged.



Region around the “hole” has one less electron and thus is positively charged.

The positively charged “hole” can move throughout the crystal (really it is the valance electrons jumping from atom to atom that creates the hole motion).

# Summary of Important terms and symbols

**Bandgap Energy:** Energy required to remove a valence electron and allow it to freely conduct.

**Intrinsic Semiconductor:** A “native semiconductor” with no dopants. Electrons in the conduction band equal holes in the valence band. The concentration of electrons (=holes) is the intrinsic concentration,  $n_i$ .

**Extrinsic Semiconductor:** A doped semiconductor. Many electrical properties controlled by the dopants, not the intrinsic semiconductor.

**Donor:** An impurity added to a semiconductor that adds an additional electron not found in the native semiconductor.

**Acceptor:** An impurity added to a semiconductor that adds an additional hole not found in the native semiconductor.

**Dopant:** Either an acceptor or donor.

**N-type material:** When electron concentrations ( $n$ =number of electrons/cm<sup>3</sup>) exceed the hole concentration (normally through doping with donors).

**P-type material:** When hole concentrations ( $p$ =number of holes/cm<sup>3</sup>) exceed the electron concentration (normally through doping with acceptors).

**Majority carrier:** The carrier that exists in higher population (ie  $n$  if  $n > p$ ,  $p$  if  $p > n$ )

**Minority carrier:** The carrier that exists in lower population (ie  $n$  if  $n < p$ ,  $p$  if  $p < n$ )

Other important terms (among others): Insulator, semiconductor, metal, amorphous, polycrystalline, crystalline (or single crystal), lattice, unit cell, primitive unit cell, zincblende, lattice constant, elemental semiconductor, compound semiconductor, binary, ternary, quaternary, atomic density, Miller indices, various notations, etc...

# Carrier Movement in Free Space

## Newton's second law

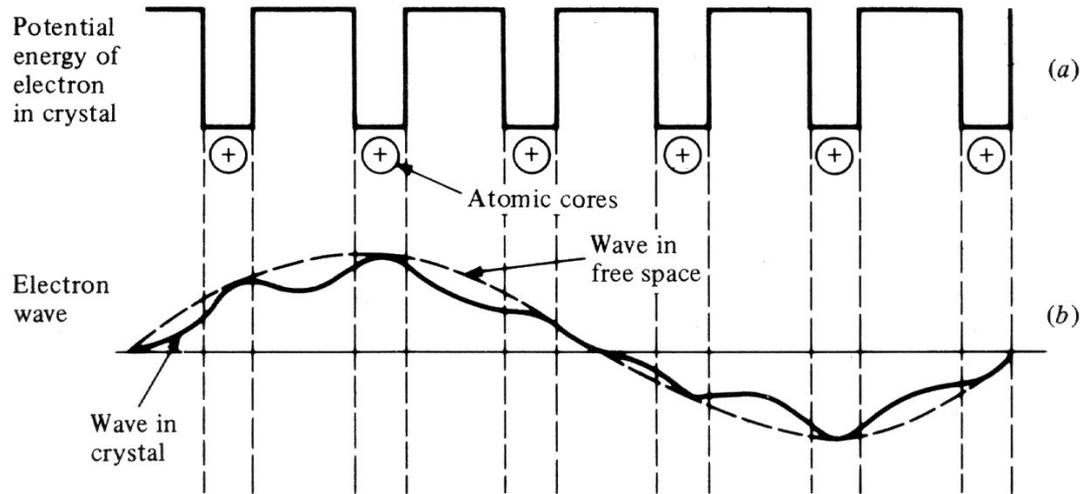
$$F = -qE = m_o \frac{dv}{dt}$$

$F \equiv$  force,  $v \equiv$  velocity,  $t \equiv$  time,

$q \equiv$  electronic charge,  $m_o \equiv$  electron mass

# Carrier Movement Within the Crystal

- Electron is a quasi-particle that behaves as a “wave” due to quantum mechanical effects.
- The electron “wavelength” is perturbed by the crystal's periodic potential.



**FIGURE 1-11**  
Representation of motion of electron wave in crystal potential. (After Wolfendale [3].)

# Carrier Movement Within the Crystal

$$F = -qE = m_n^* \frac{dv}{dt}$$

$F \equiv$  force,  $v \equiv$  velocity,  $t \equiv$  time,

$q \equiv$  electronic charge,

$m_n^* \equiv$  electron effective mass

$$F = qE = m_p^* \frac{dv}{dt}$$

$F \equiv$  force,  $v \equiv$  velocity,  $t \equiv$  time,

$q \equiv$  electronic charge,

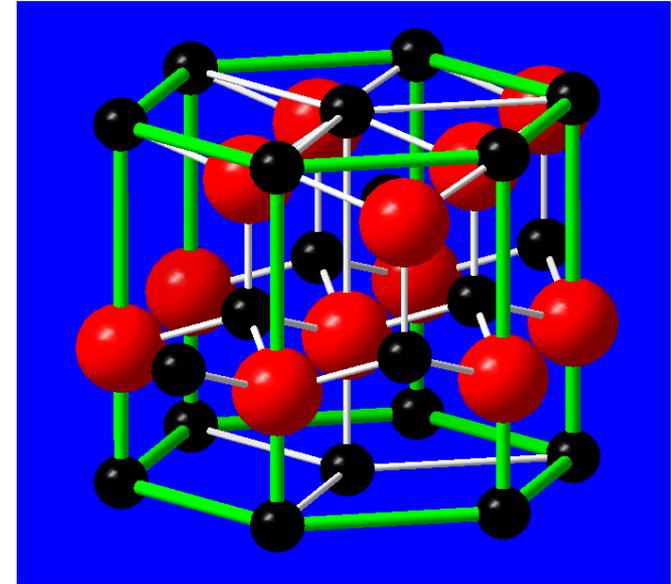
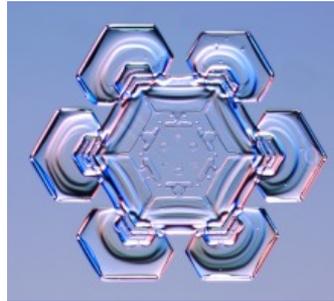
$m_p^* \equiv$  hole effective mass

**Table 2.1** Density of States Effective Masses at 300 K.

Material	$m_n^*/m_0$	$m_p^*/m_0$
Si	1.18	0.81
Ge	0.55	0.36
GaAs	0.066	0.52

Ge and GaAs have “lighter electrons” than Si  
which results in faster devices

# Crystalline Order



Water Molecules,  $H_2O$ , forming “Snowflakes”

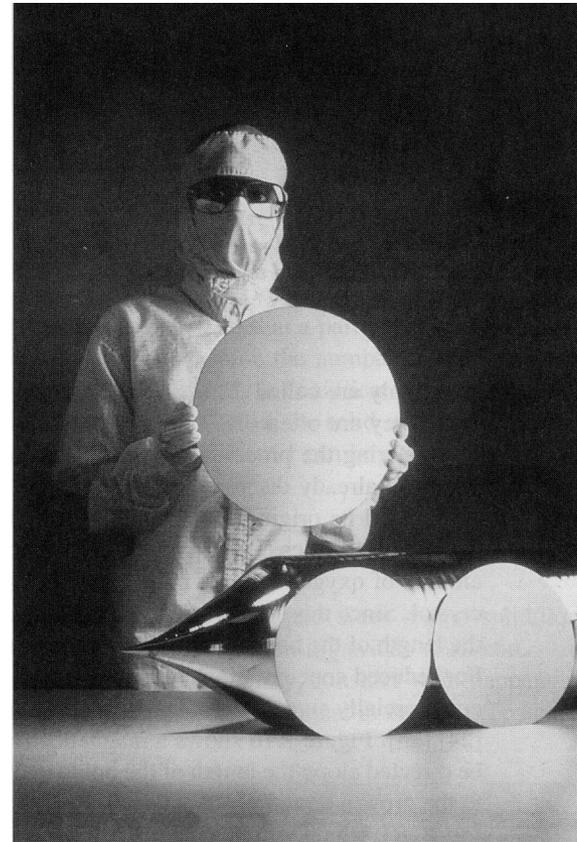
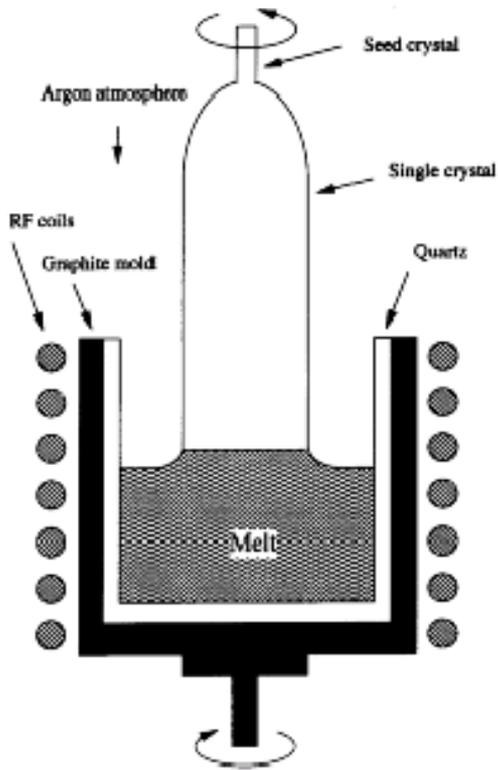
Atoms forming a  
“Semiconductor”

**Need two volunteers...** (demo on how a crystal forms naturally due to repulsive electronic bonds)

# **How are semiconductors produced?**

# Crystal Growth: How do we get “Single Crystalline Material”?

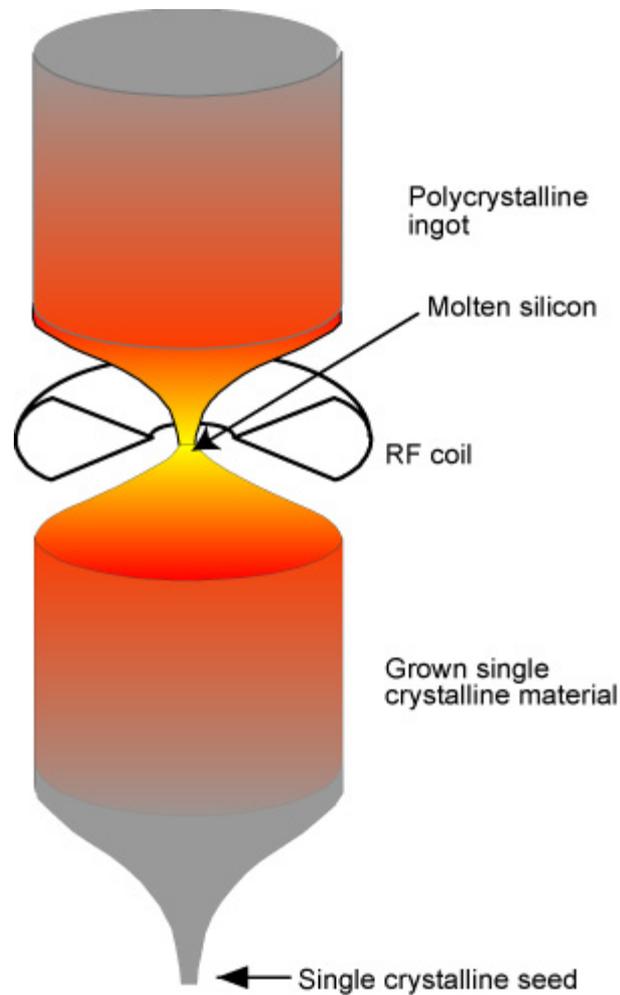
The vast majority of crystalline silicon produced is grown by the Czochralski growth method. In this method, a single crystal seed wafer is brought into contact with a liquid Silicon charge held in a crucible (typically  $\text{SiO}_2$  but may have a lining of silicon-nitride or other material). The seed is pulled out of the melt, allowing Si to solidify. The solidified material bonds to the seed crystal in the same atomic pattern as the seed crystal.



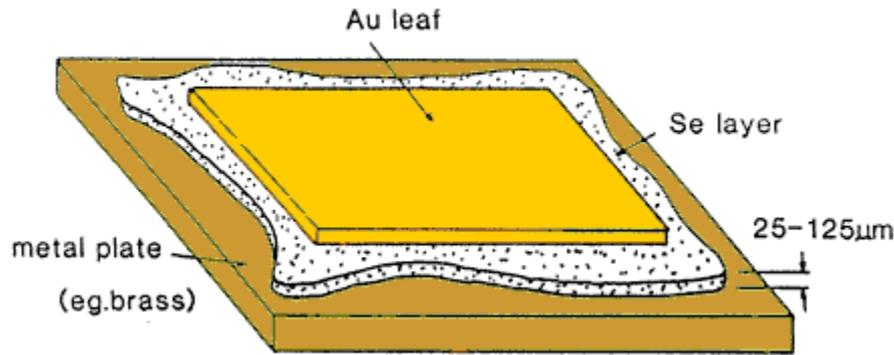
Schematic representation of the Czochralski (a) and float-zone (b) single-crystal growth techniques.

# Production of Solar Cell Grade Semiconductors

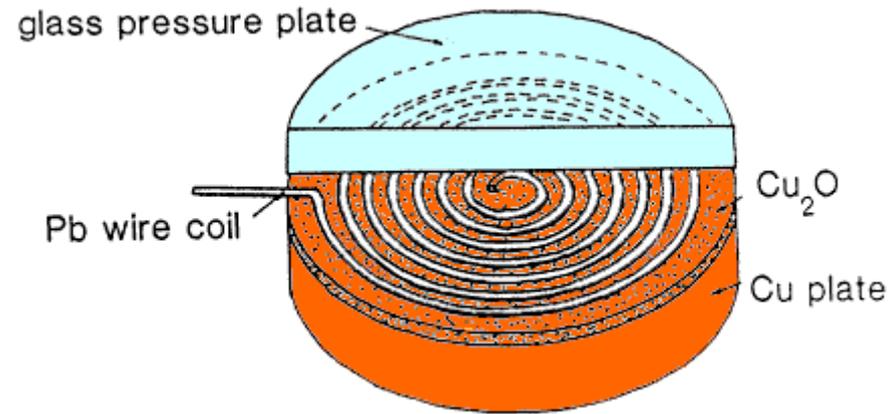
## Float Zone Refinement for Ultra-High grade Silicon



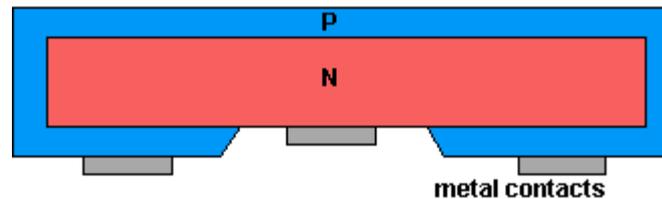
# Production of Solar Cell Grade Semiconductors



First solid Thin-film selenium solar cell demonstrated by Fritts in 1883.



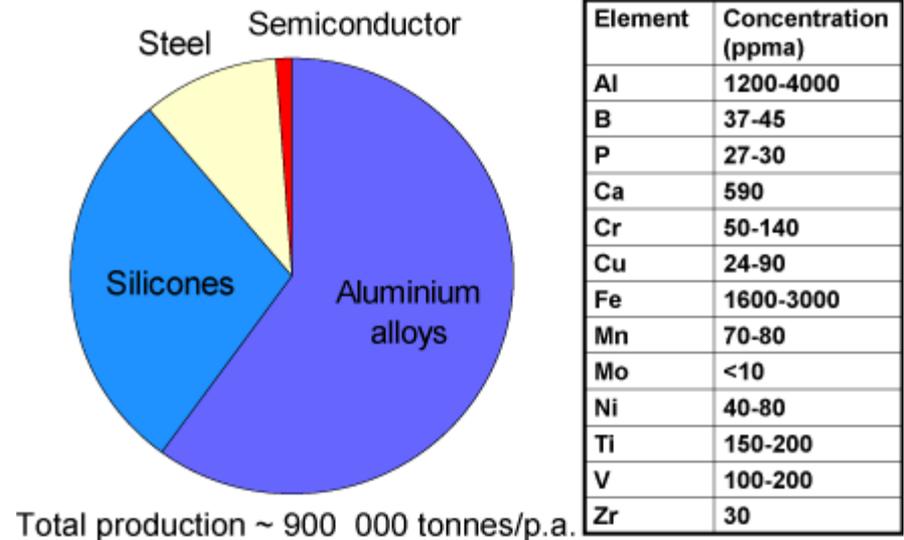
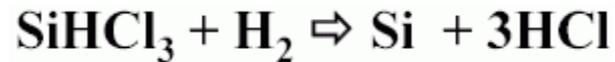
Early Grondahl-Geiger copper-cuprous oxide photovoltaic cell (circa 1927).



Structure of the first “modern” Si solar cell. 6% efficiency (~15x improvement at the time).

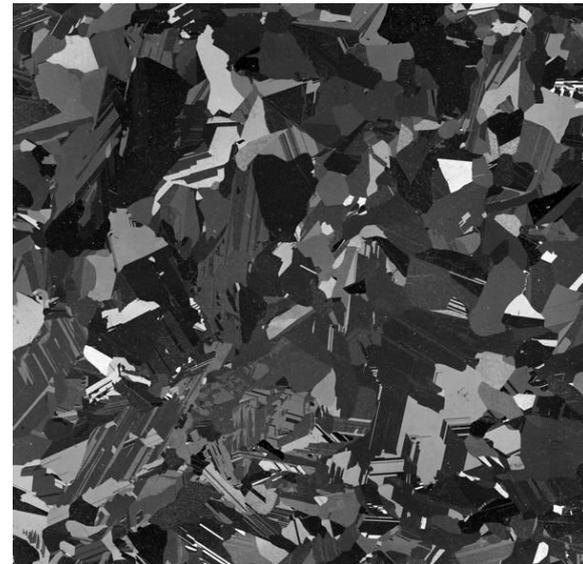
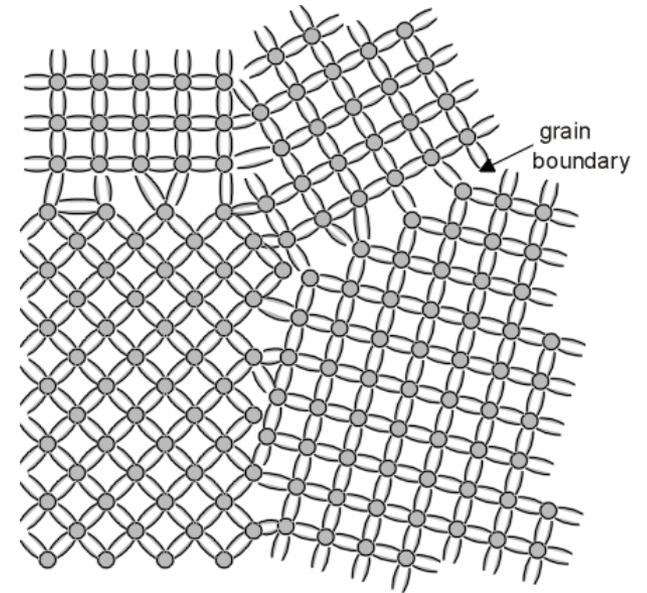
Chapin, D.M., Fuller, C.S. and Pearson, G.L., "A New Silicon P-N Junction Photocell for Converting Solar Radiation into Electrical Power", *Journal of Applied Physics*, Vol. 25, pp. 676-677, 1954.

# Production of Solar Cell Grade Semiconductors

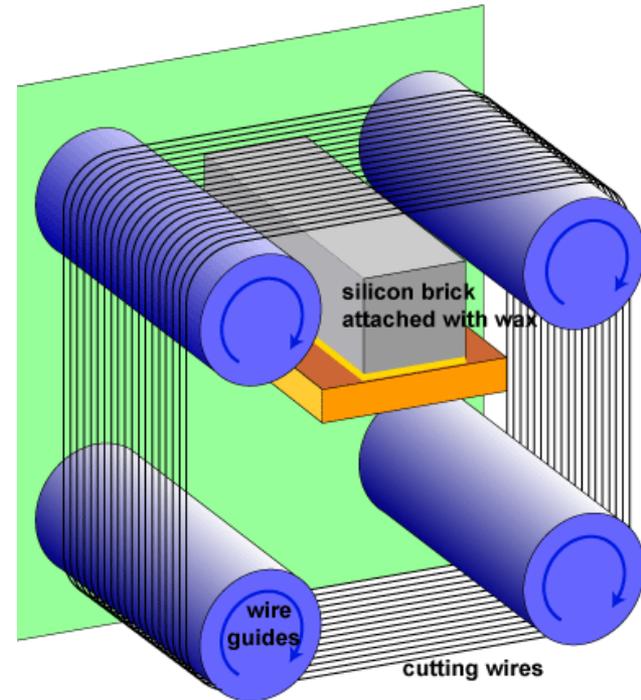


Descriptor	Symbol	Grain Size	Common Growth Techniques
Single crystal	sc-Si	>10cm	Czochralski (CZ) float zone (FZ)
Multicrystalline	mc-Si	1mm-10cm	Cast, sheet, ribbon
Polycrystalline	pc-Si	1 $\mu$ m-1mm	Chemical-vapour deposition
Microcrystalline	$\mu$ c-Si	<1 $\mu$ m	Plasma deposition

# Production of Solar Cell Grade Semiconductors

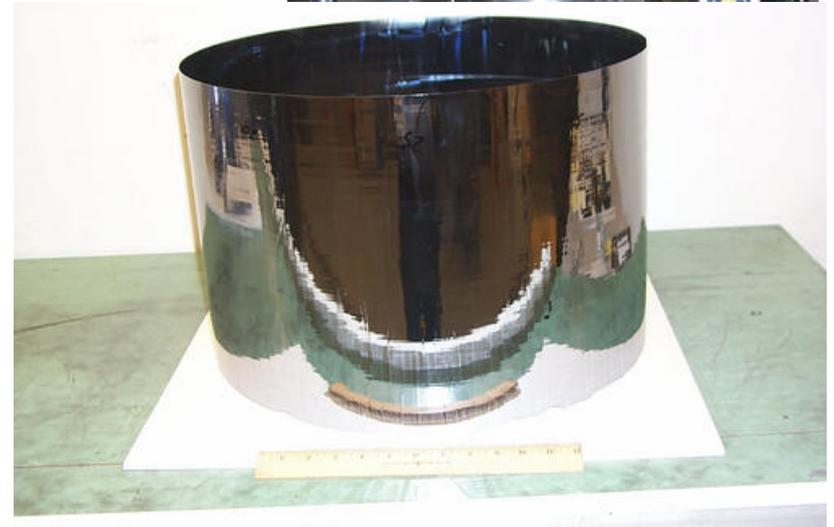
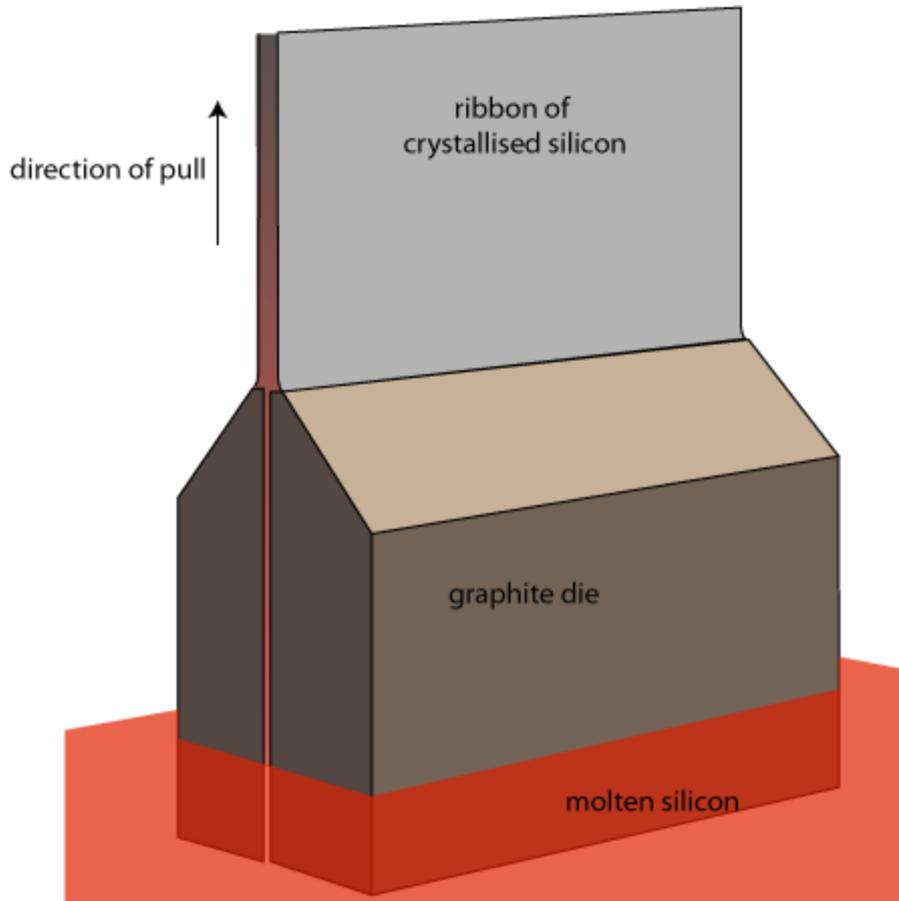


# Production of Solar Cell Grade Semiconductors



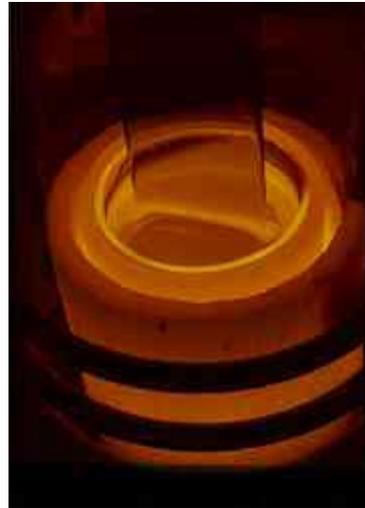
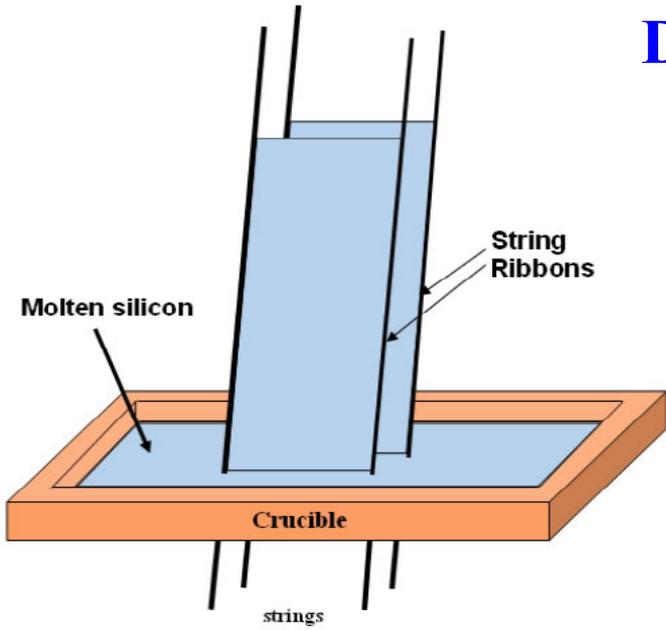
# Production of Solar Cell Grade Semiconductors

## Edge Film Grown



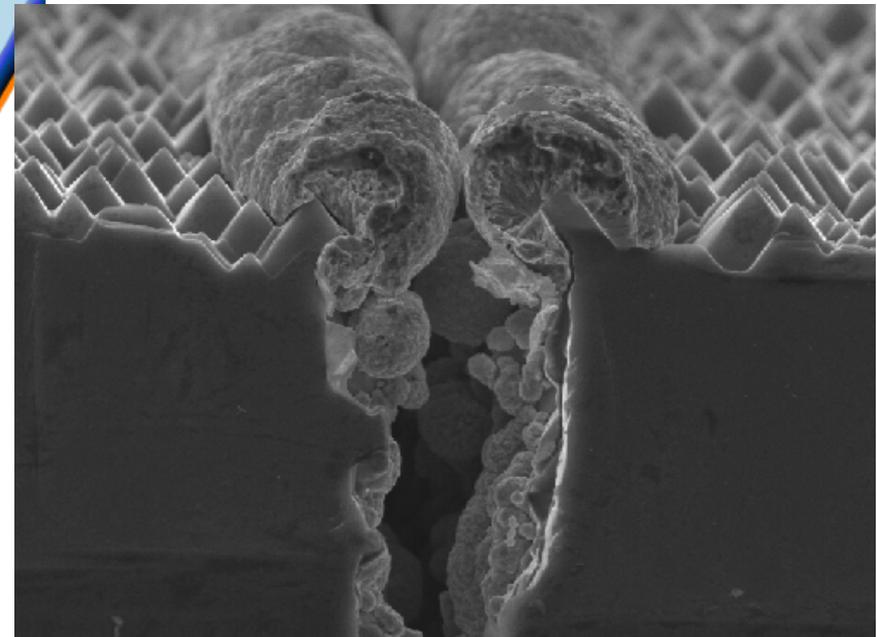
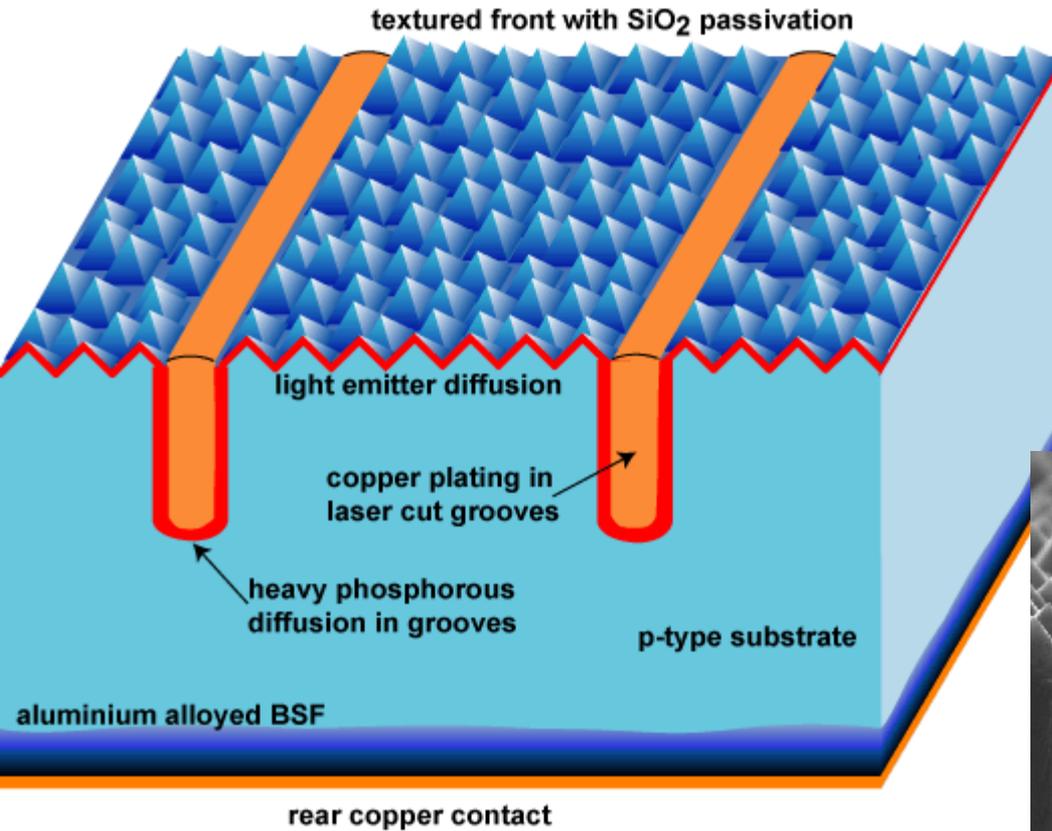
# Production of Solar Cell Grade Semiconductors

## Dendritic Web Silicon



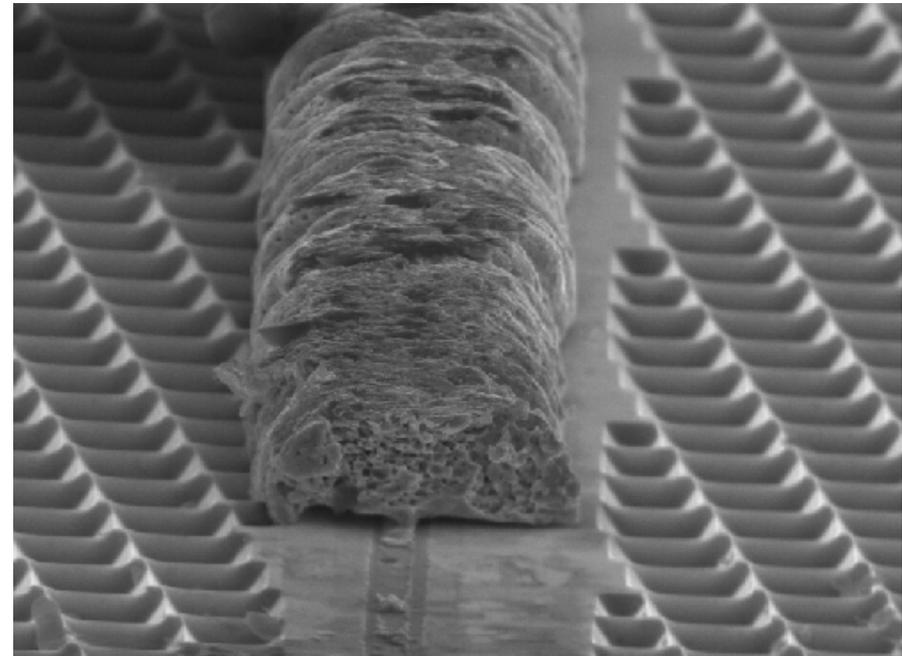
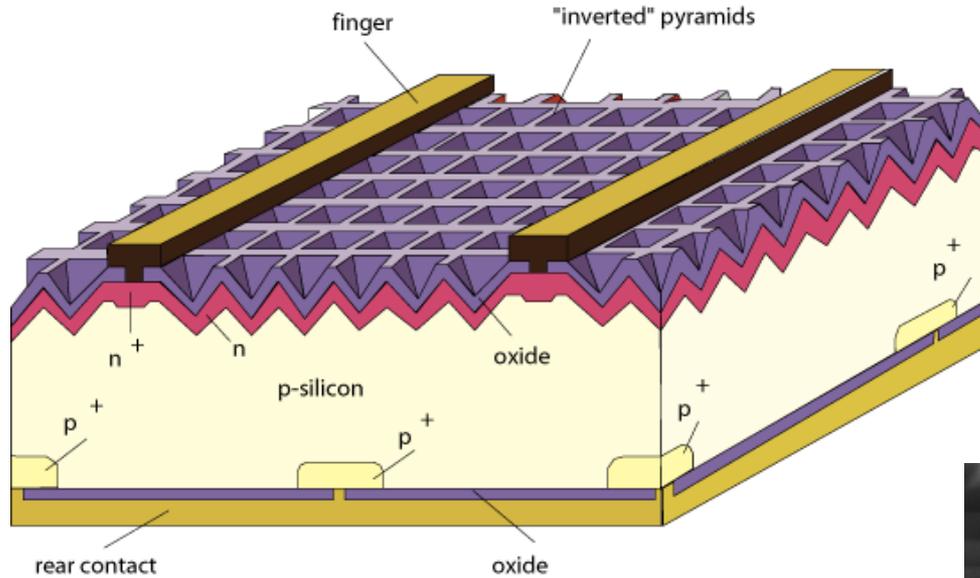
# Production of Solar Cell Grade Semiconductors

## High performance Laser Grooved, plated and random surface textured Si Solar Cells



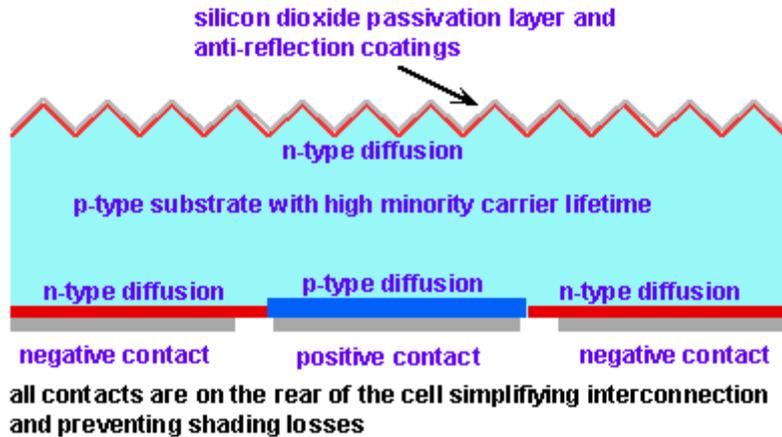
# Production of Solar Cell Grade Semiconductors

## High performance Inverted Pyramid Si Solar Cells with minimal metal-semiconductor contact area



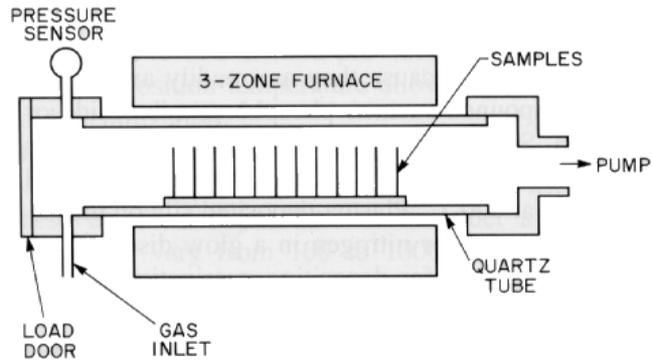
# Production of Solar Cell Grade Semiconductors

## High performance Back Contact Si Solar Cells with minimal shadowing and minimal metal-semiconductor contact area

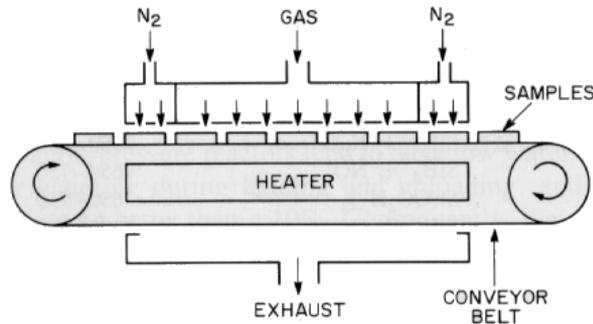


# Chemical Vapor Deposition

Chemical gas sources are thermally, optically, or electrically (plasma) reacted with a surface to “leave” behind deposits with reaction byproducts pumped out of the reaction tube or vacuum chamber.



(a)



(b)

**FIGURE 1**

Schematic diagrams of CVD reactors: (a) Hot-wall, reduced-pressure reactor. (b) Continuous, atmospheric-pressure reactor.



# Four Basic CVD Reactors

## 1.) Atmospheric Pressure CVD (APCVD)

Advantages: High deposition rates, simple, high throughput

Disadvantages: Poor uniformity, purity is less than LPCVD

Used mainly for thick oxides.

## 2.) Low Pressure CVD (LPCVD at ~0.2 to 20 torr)

Advantages: Excellent uniformity, purity

Disadvantages: Lower (but reasonable) deposition rates than APCVD

Used for polysilicon deposition, dielectric layer deposition, and doped dielectric deposition.

## 3.) Metal Organic CVD (MOCVD)

Advantages.: Highly flexible—> can deposit semiconductors, metals, dielectrics

Disadvantages: **HIGHLY TOXIC!**, Very expensive source material. Environmental disposal costs are high.

Uses: Dominates optical (but not electronic) III-V technology, some metallization processes (W plugs and Cu)

## 4.) Plasma Enhanced CVD

Plasmas are used to force reactions that would not be possible at low temperature.

Advantages.: Uses low temperatures necessary for rear end processing.

Disadvantages: Plasma damage typically results.

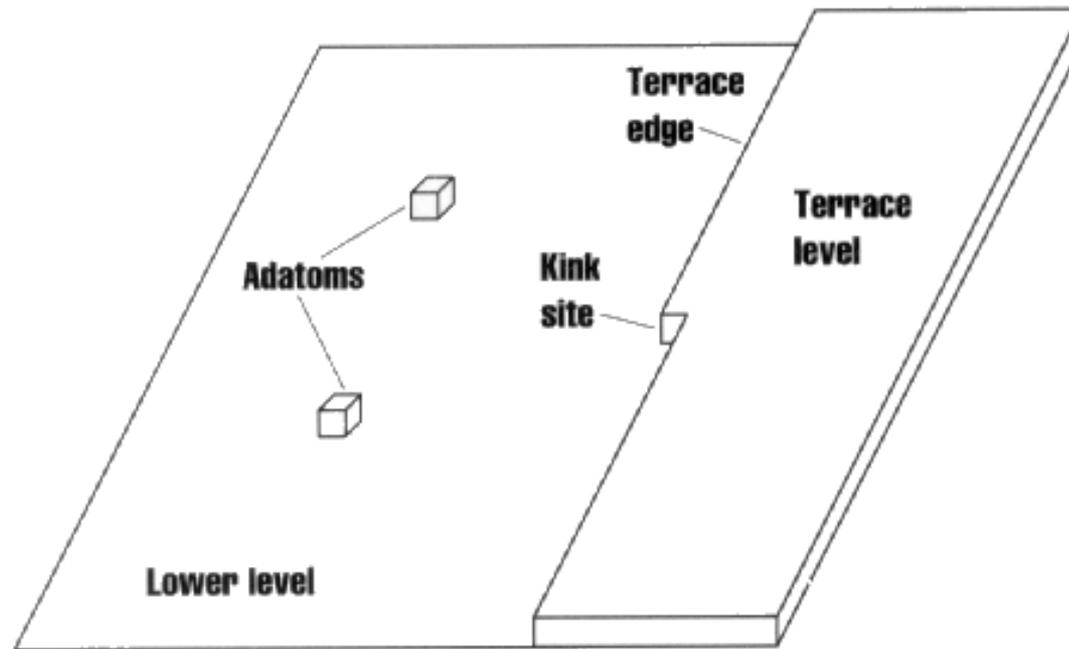
Used for dielectrics coatings.

# Epitaxy

## Single Crystal Semiconductors (Epitaxy)

We can grow\* crystalline semiconductors by raising the temperature to allow more surface migration and by using a crystalline substrate (Si, GaAs, InP wafer, etc...)

====> Single crystal material mimicking the crystal structure of the layers below it.



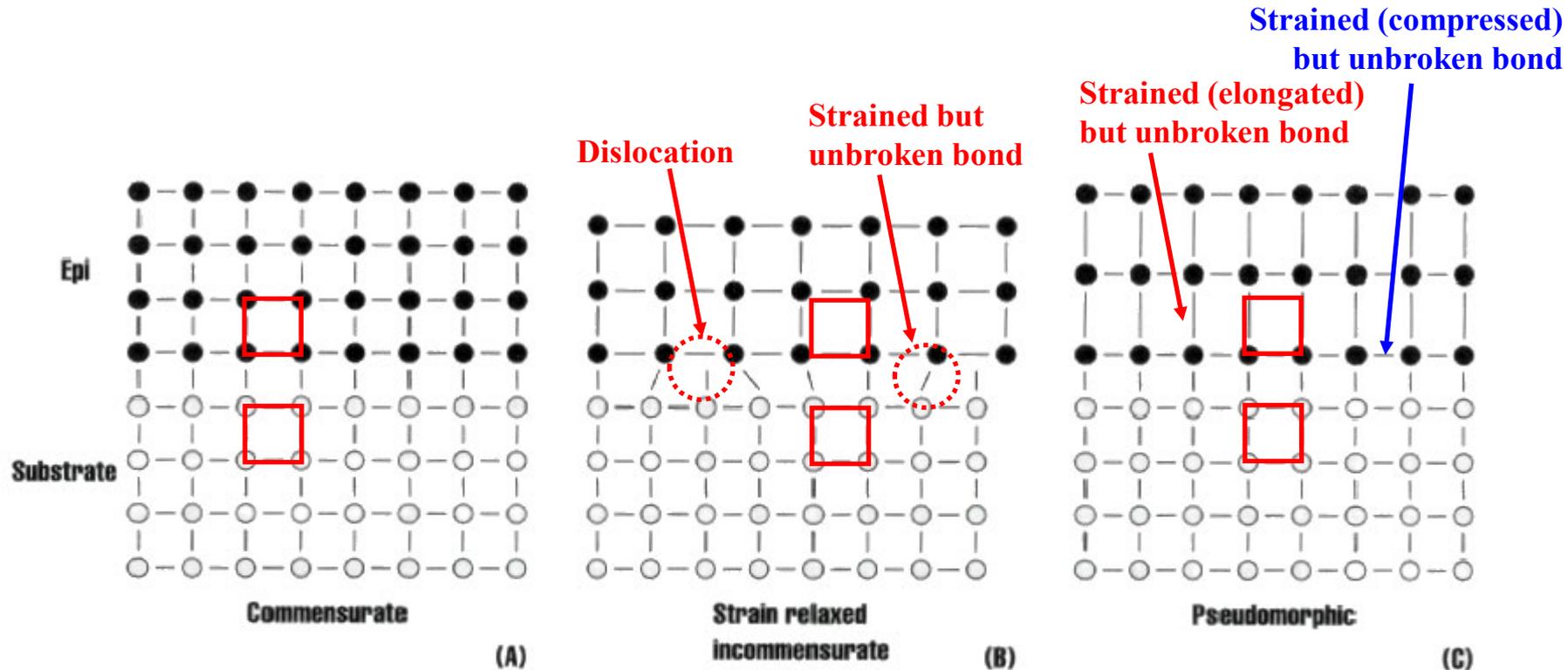
**Figure 14-32** A microscopic view of a semiconductor surface during MBE growth or evaporation.

\*Instead of the word deposit, we use “grow” to describe the tendency of the deposited material to mimic the crystal structure of crystalline substrate material.

# Epitaxy

## Importance of lattice mismatch

The lattice constant of the epitaxially grown layer needs to be close to the lattice constant of the substrate wafer. Otherwise the bonds can not stretch far enough and dislocations will result.



**Figure 14-15** Epitaxial growth processes can be divided into (a) commensurate, (b) strain relaxed incommensurate, and (c) incommensurate but pseudomorphic.

# Epitaxy

## Importance of lattice mismatch

The lattice constant of the epitaxially grown layer needs to be close to the lattice constant of the substrate wafer. Otherwise the bonds can not stretch far enough and dislocations will result.

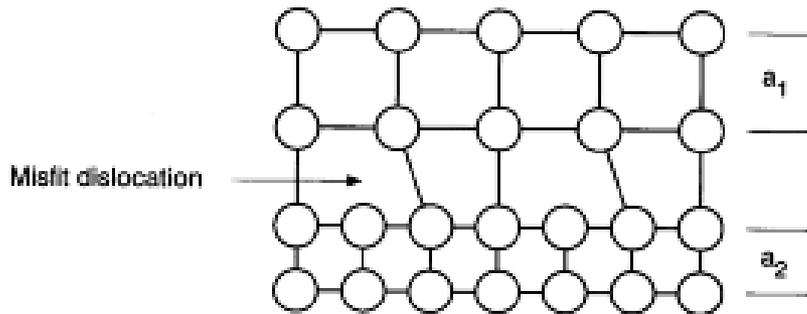


Figure 2.7 Misfit dislocation schematic.

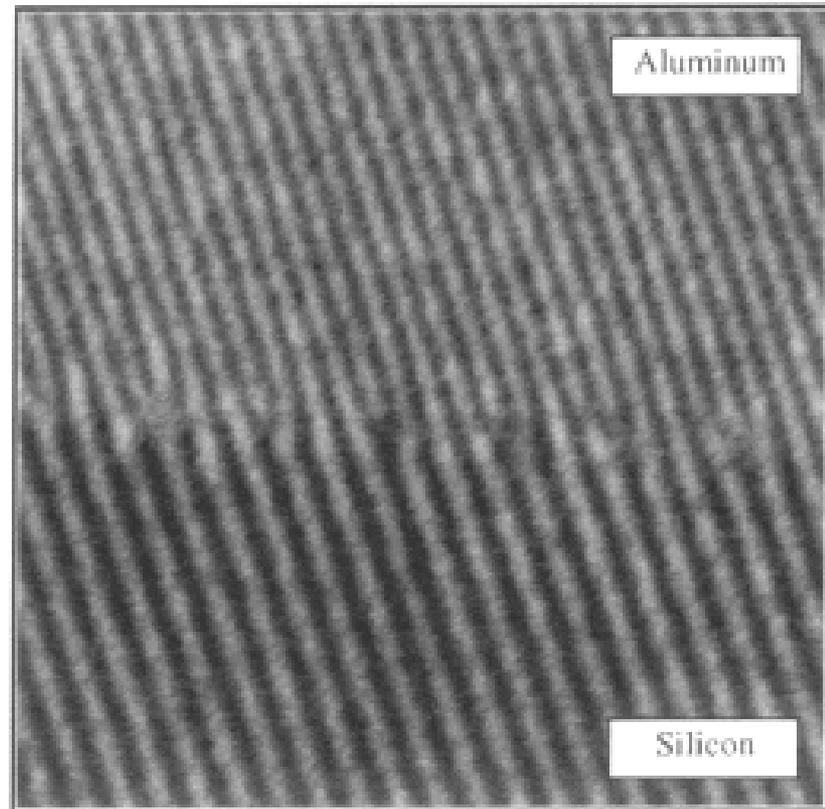


Figure 2.8 A TEM comparable to the schematic of Figure 2.7 that shows the (111) planes of aluminum epitaxially overgrown on silicon and the (111) planes of the silicon substrate.

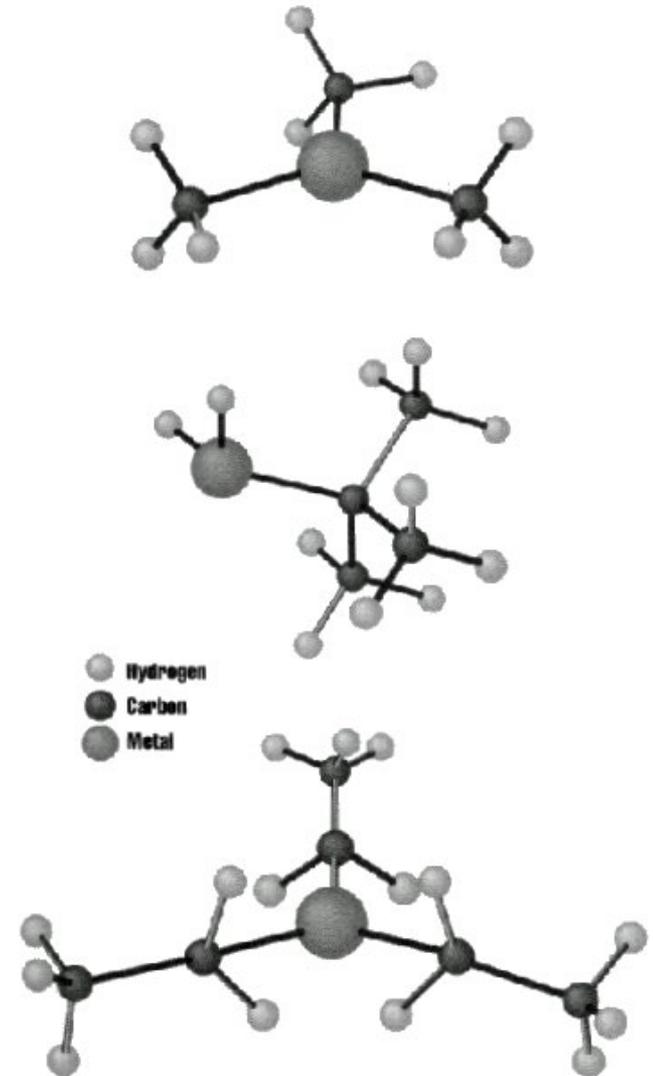
# MOCVD

Primarily used for II-VI, and III-V semiconductors, special metallic oxides and metals.

## Metal Organic Chemical Vapor Deposition (MOCVD)

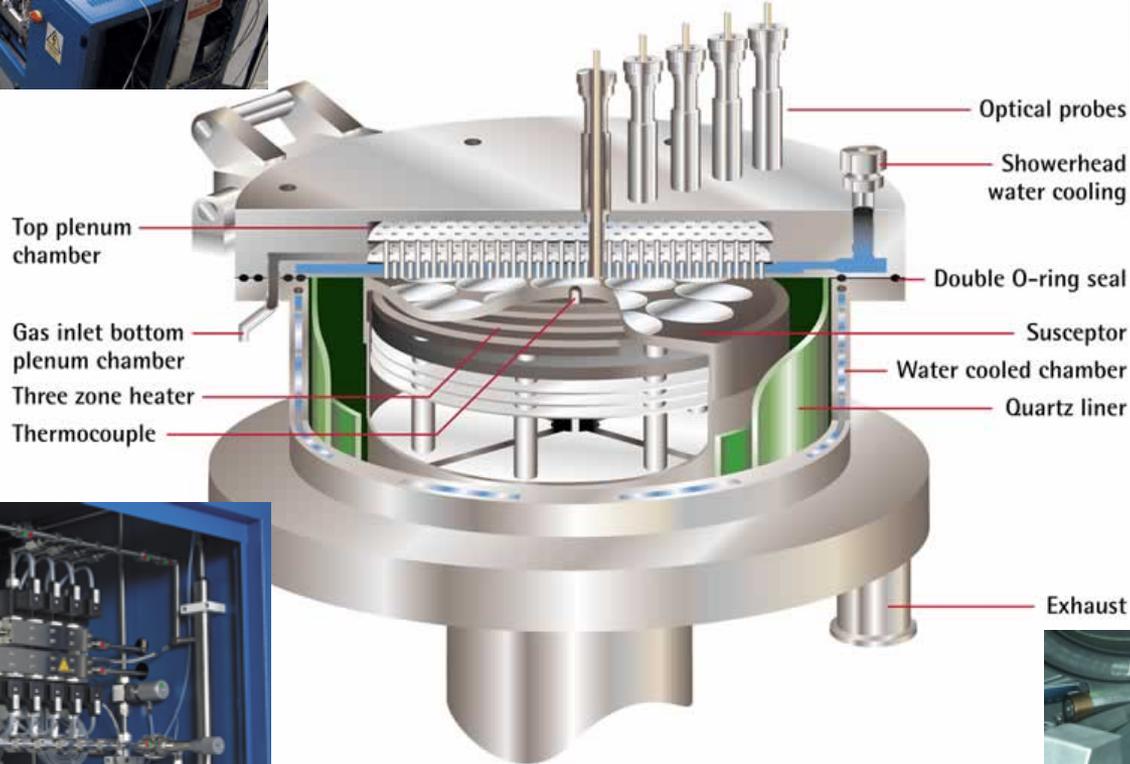
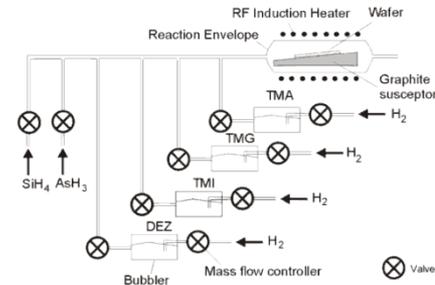
- Many materials that we wish to deposit have very low vapor pressures and thus are difficult to transport via gases.
- One solution is to chemically attach the metal (Ga, Al, Cu, etc...) to an organic compound that has a very high vapor pressure. Organic compounds often have very high vapor pressure (for example, alcohol has a strong odor).
- The organic-metal bond is very weak and can be broken via thermal means on wafer, depositing the metal with the high vapor pressure organic being pumped away.
- Care must be taken to insure little of the organic byproducts are incorporated. Carbon contamination and unintentional Hydrogen incorporation are sometimes a problem.

Human Hazard: As the human body absorbs organic compounds very easily, the metal organics are very easily absorbed by humans. Once in the body, the weak metal-organic bond is easily broken, thus, poisoning the body with heavy metals that often can not be easily removed by normal bodily functions. In extreme cases, blood transfusion is the only solution (if caught in time).



**Figure 14-19** Examples of common organometallics used in MOCVD include (from top to bottom): trimethylgallium, tetrabutylarsine, and triethylgallium.

# Commercial Thomas Swan® MOCVD



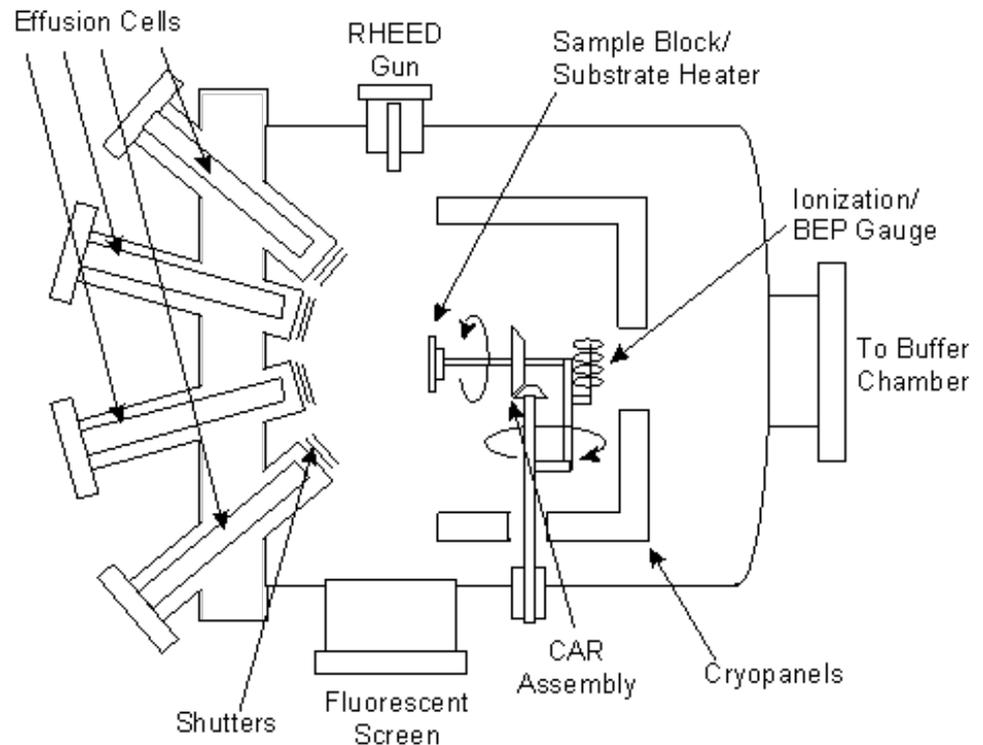
# MBE

## Molecular Beam Epitaxy (MBE)

Dominates III-V electronic market and strong competitor in upper end LASER market

Offers the highest purity material (due to UHV conditions) and the best layer control (almost any fraction of an atomic layer can be deposited and layers can be sequenced one layer at a time (for example Ga then As then Ga etc...)).

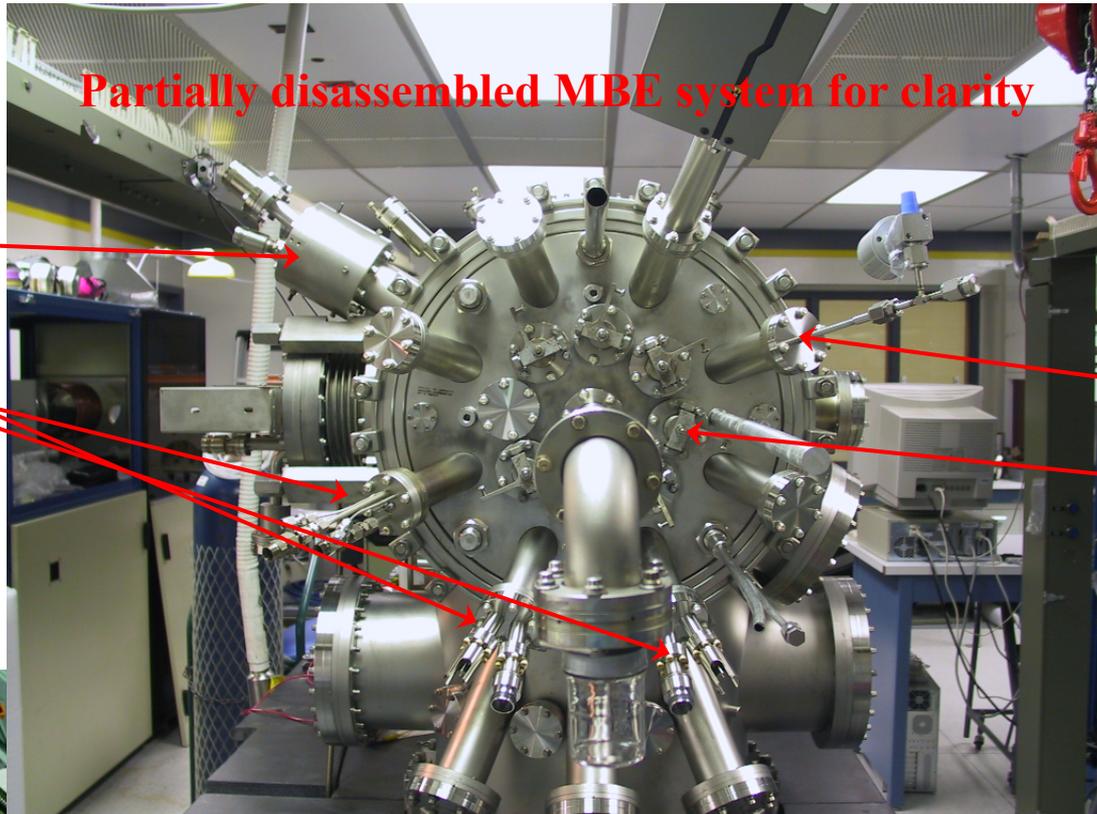
- In an UHV chamber, ultra high purity materials are evaporated.
- Because of the very low pressure, the mean free path is very long (can be hundreds of meters). Thus, the evaporated material travels in a straight line (a molecular beam) toward a hot substrate.
- Once on the substrate, the atom or molecule moves around until it finds an atomic site to chemically bond to.
- Shutters can be used to turn the beam flux on and off
- The flux of atoms/molecules is controlled by the temperature of the “effusion cell” (evaporation source).





# MBE

Partially disassembled MBE system for clarity

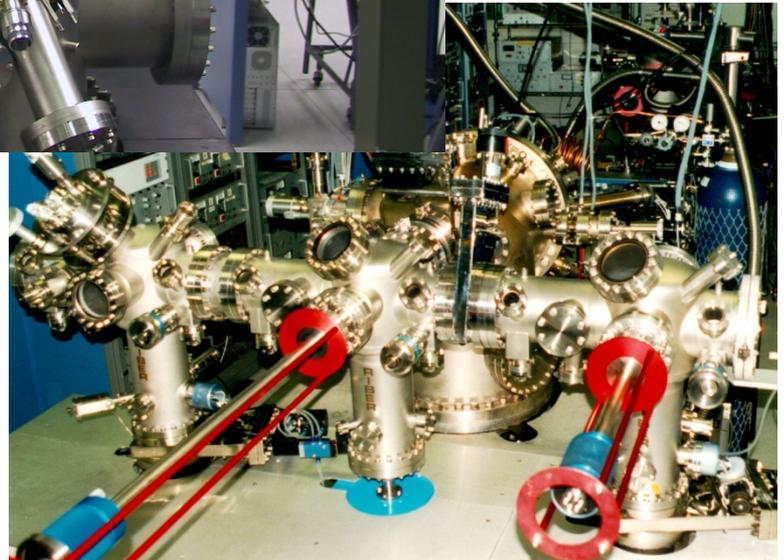
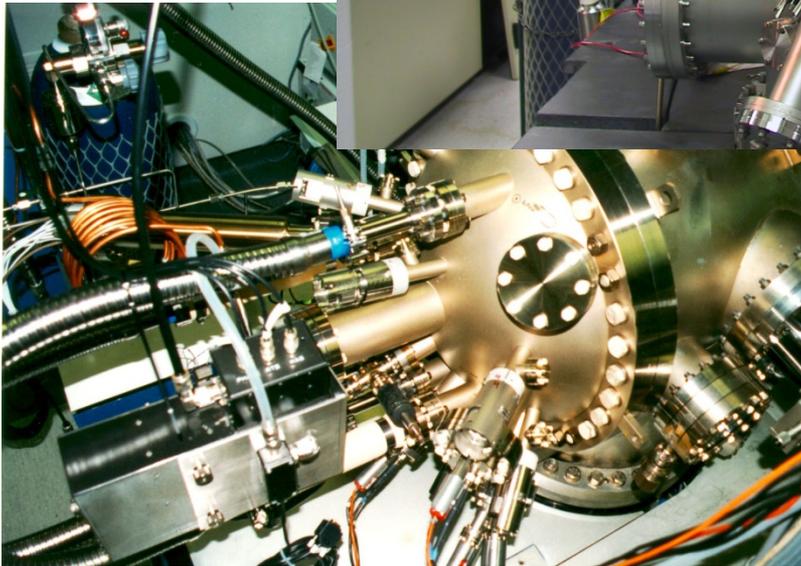


RHEED Gun

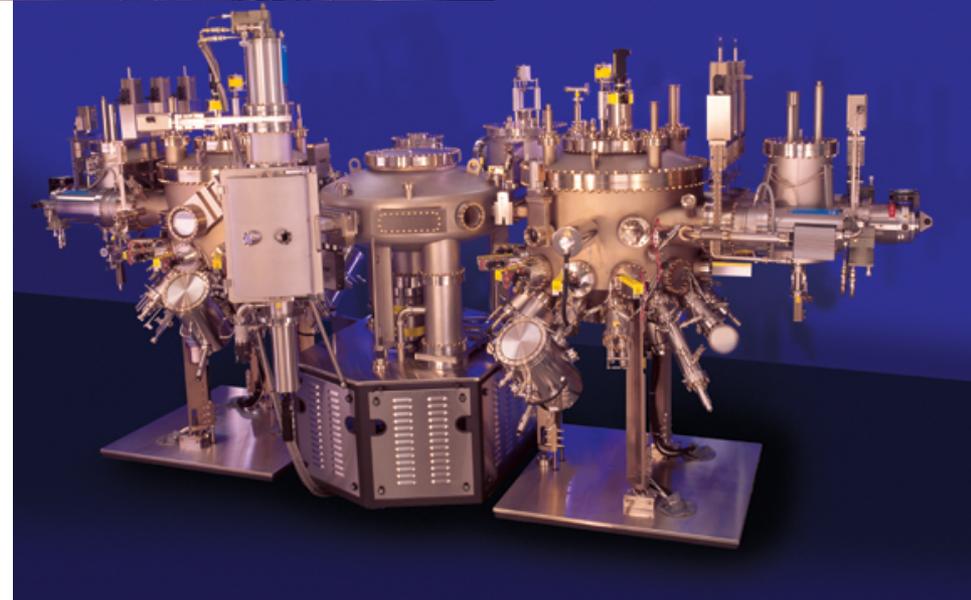
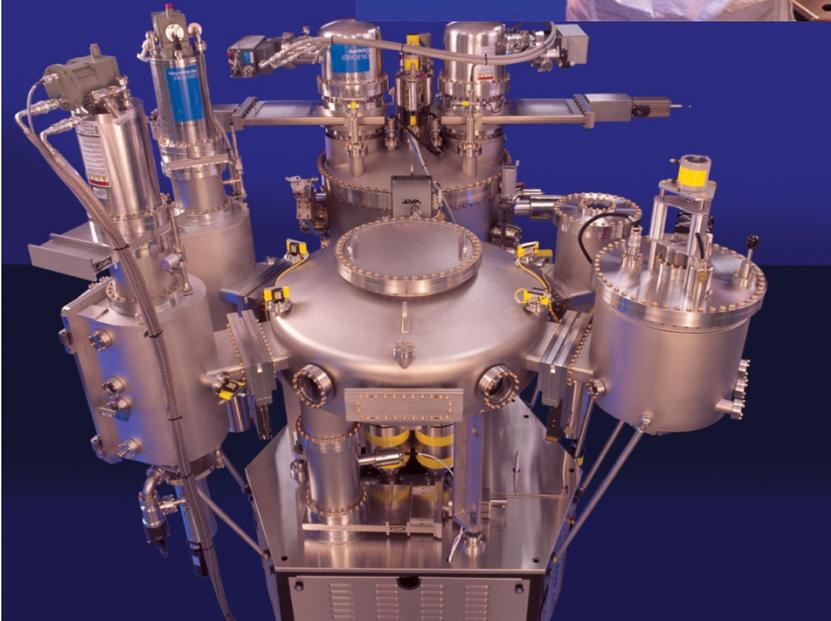
Effusion Furnaces

Gas Source (oxygen)

Shutter mechanism



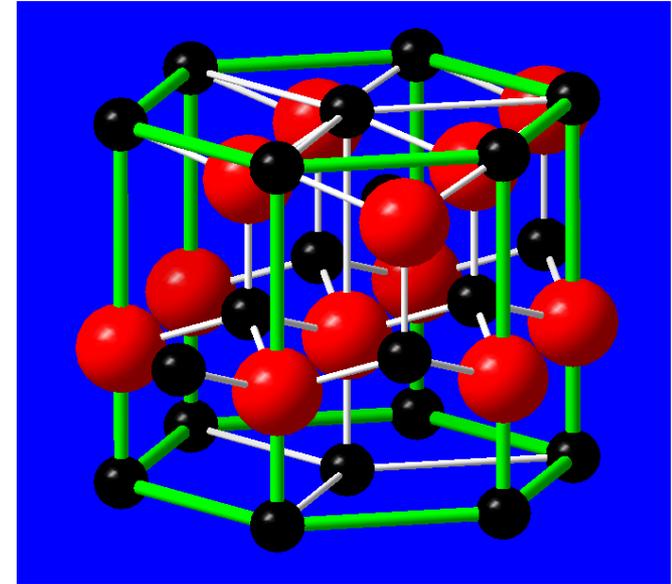
# Commercial Veeco® MBE



# Crystalline Order



Water Molecules,  $H_2O$ , forming “Snowflakes”



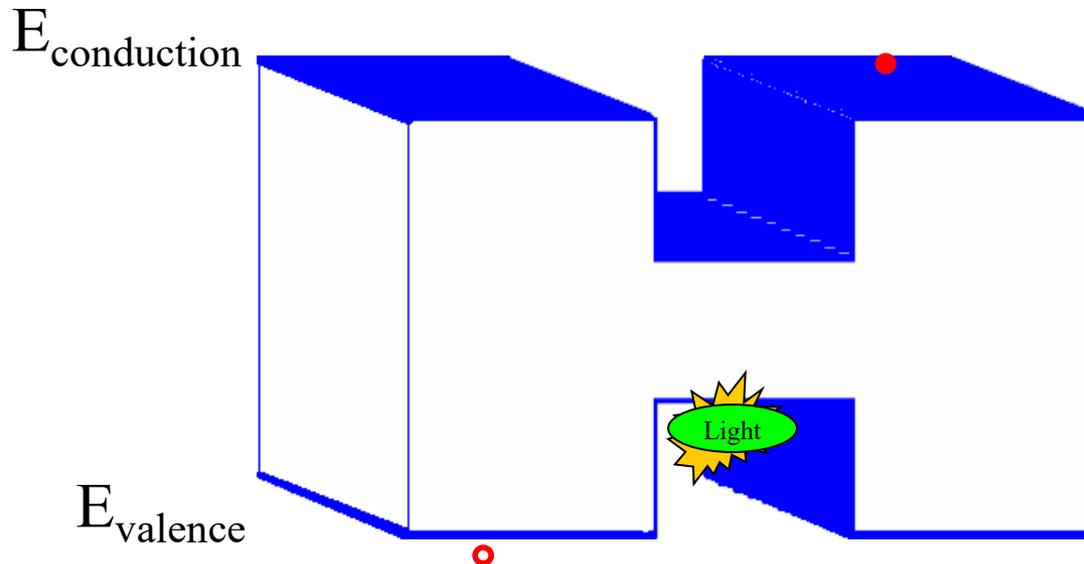
Atoms forming a  
“Semiconductor”

**Need two volunteers...** (demo on how a crystal forms naturally due to repulsive electronic bonds)

# Heterojunction Materials

Compound Semiconductors allow us to perform “Bandgap Engineering” by changing the energy bandgap as a function of position. This allows the electrons to see “engineered potentials” that “guide” electrons/holes in specific directions or even “trap” them in specific regions of devices designed by the electrical engineer.

Example: Consider the simplified band diagram of a GaN/ Ga<sub>0.75</sub>In<sub>0.25</sub>N/ GaN LED structure. Electrons and holes can be “localized” (trapped) in a very small region – enhancing the chance they will interact (recombine). This is great for light emitters!



# How do we produce these Energy Engineered Structures and Devices?

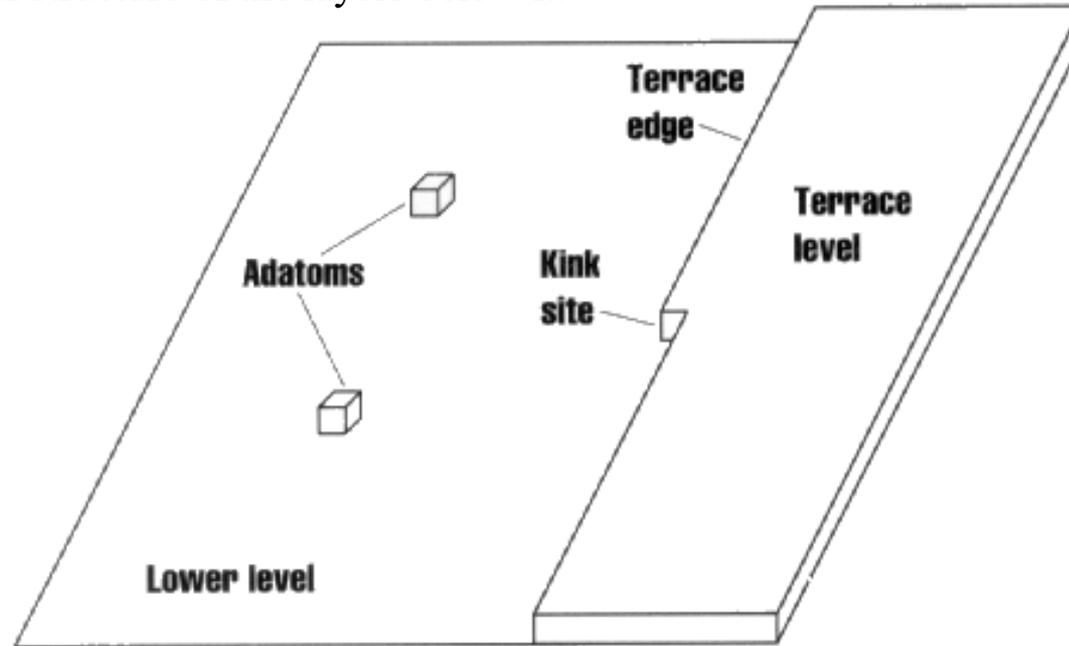
## Epitaxial Semiconductor and Dielectric deposition Techniques:

- “Epitaxial” is derived from the Greek word for skin, more specifically “thin skin”. Thin layers of materials are deposited on a substrate
- Temperature and substrate determines the physical structure of the deposited films:
  - Low Temperatures or non-crystalline substrate:
    - Materials end up with amorphous or polycrystalline materials
  - High Temperature AND Crystalline substrate
    - Need to have an existing crystalline wafer so as to “seed” the crystallization process.
    - Films that retain the substrates basic crystal structure are “Epitaxial”

# Epitaxy

## Single Crystal Semiconductors (Epitaxy)

We can grow\* crystalline semiconductors by raising the temperature to allow more atom surface migration (movement of atoms due to thermal energy) and by using a crystalline substrate (Si, GaAs, InP wafer, etc...) to act as a “template” or crystalline pattern. This results in a single crystal material mimicking the crystal structure of the layers below it.



**Figure 14-32** A microscopic view of a semiconductor surface during MBE growth or evaporation.

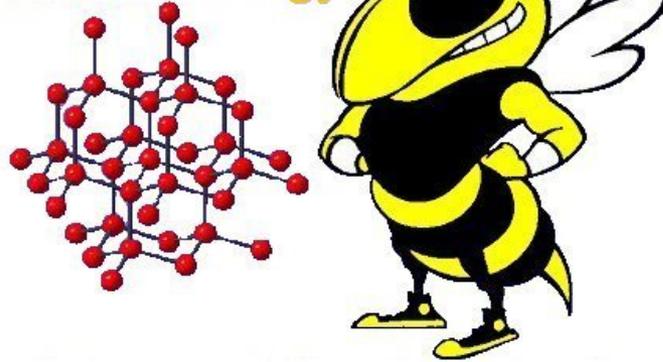
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# Advanced Semiconductor Technology Facility

# Georgia Institute of Technology

**Dr. W. Alan Doolittle**

Georgia Institute  
of Technology



**Advanced Semiconductor  
Technology Facility**

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**Georgia Institute of Technology**

**777 Atlantic Dr.**

**Atlanta, GA 30332-0250**

**Georgia Tech**

**ECE 4833 - Dr. Alan Doolittle**

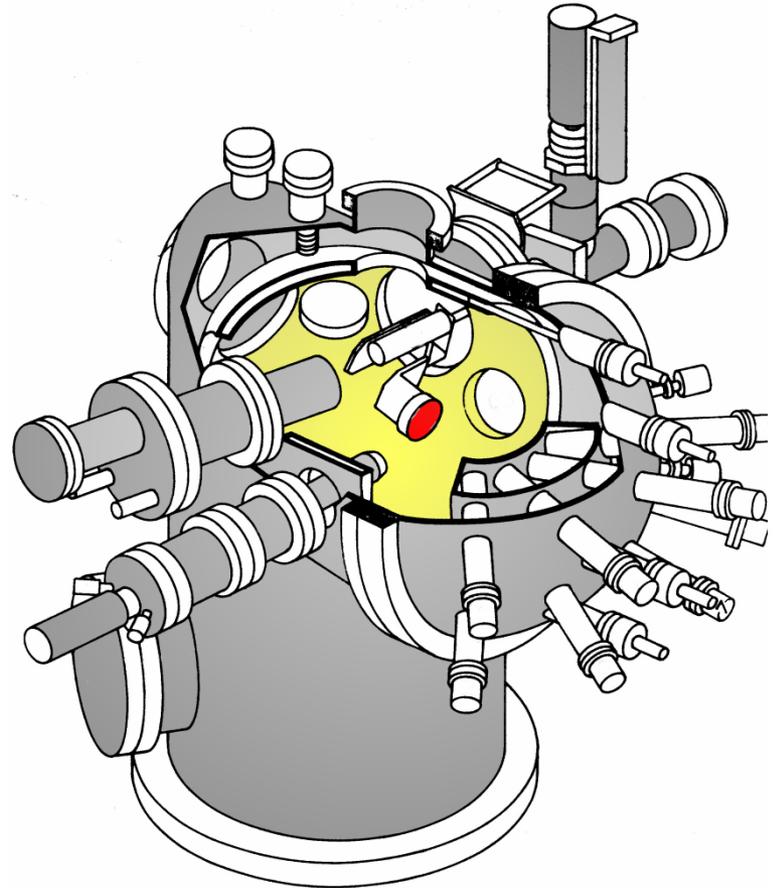
# Molecular Beam Epitaxy (MBE)

## Molecular Beam Epitaxy (MBE)

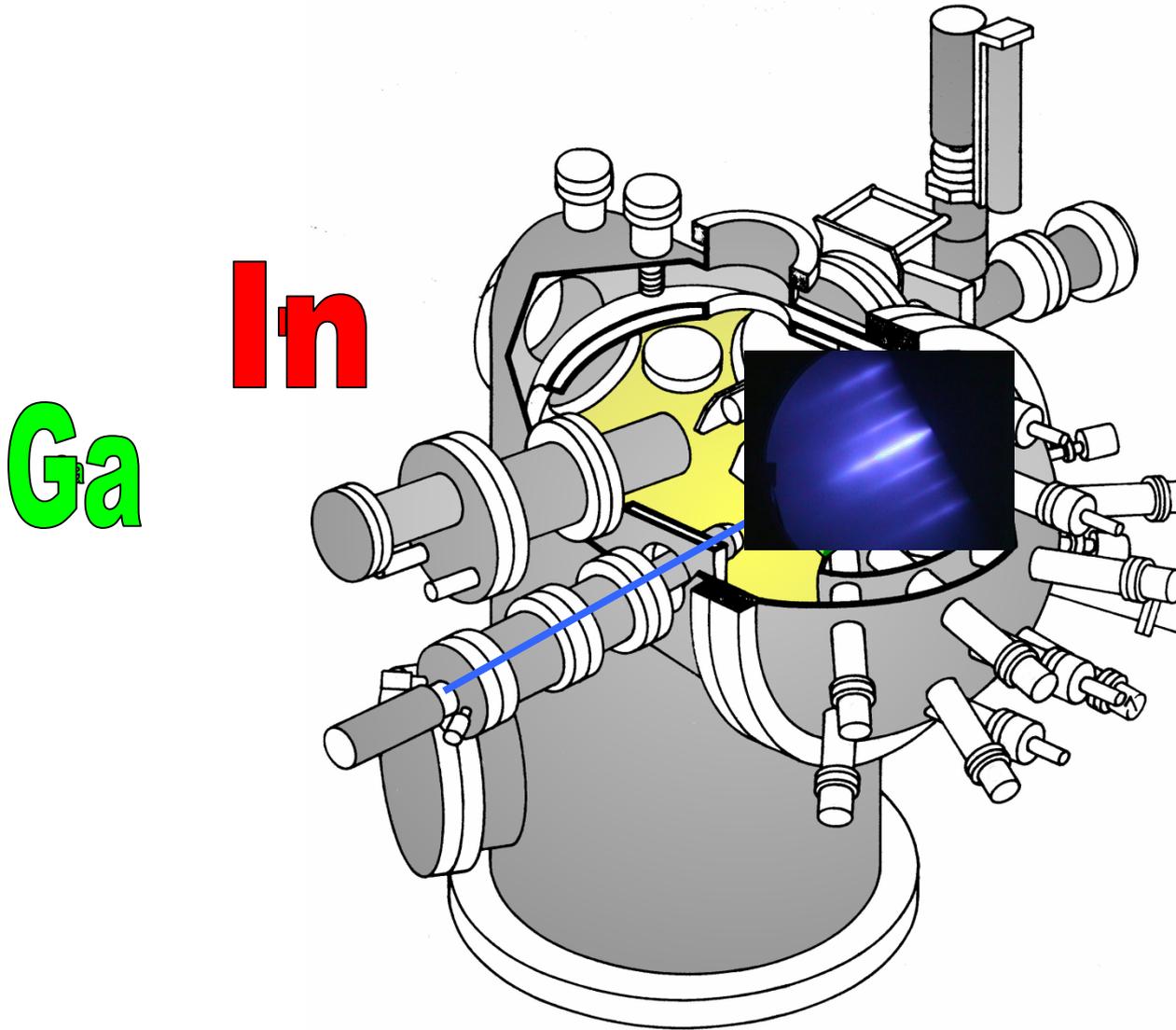
Dominates III-V electronic market and strong competitor in upper end LASER market

Offers the highest purity material (due to UHV conditions) and the best layer control (almost any fraction of an atomic layer can be deposited and layers can be sequenced one layer at a time (for example Ga then As then Ga etc...)).

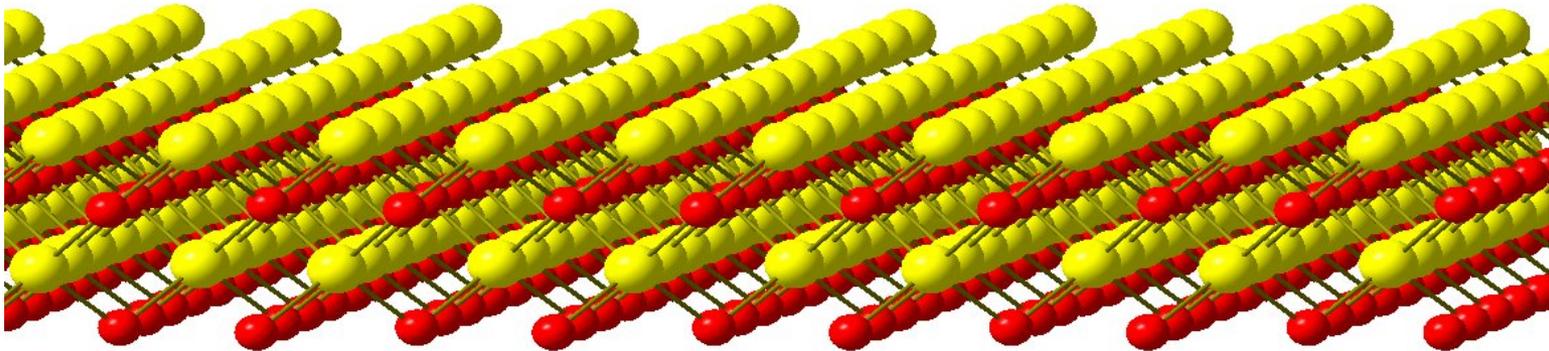
- In an UHV chamber, ultra high purity materials are evaporated.
- Because of the very low pressure, the mean free path is very long (can be hundreds of meters). Thus, the evaporated material travels in a straight line (a molecular beam) toward a hot substrate resulting in highly efficient raw materials usage.
- Once on the substrate, the atom or molecule moves around until it finds an atomic site to chemically bond to.
- Shutters can be used to turn the beam flux on and off
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# Molecular Beam Epitaxy (MBE)

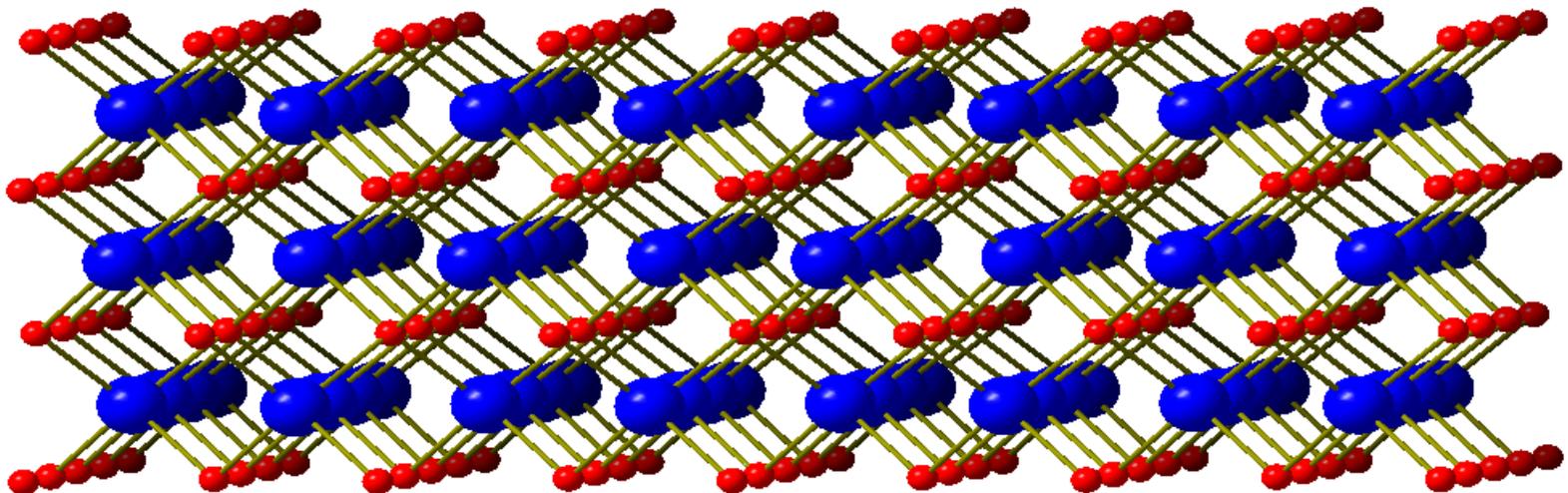


# Molecular Beam Epitaxy (MBE)



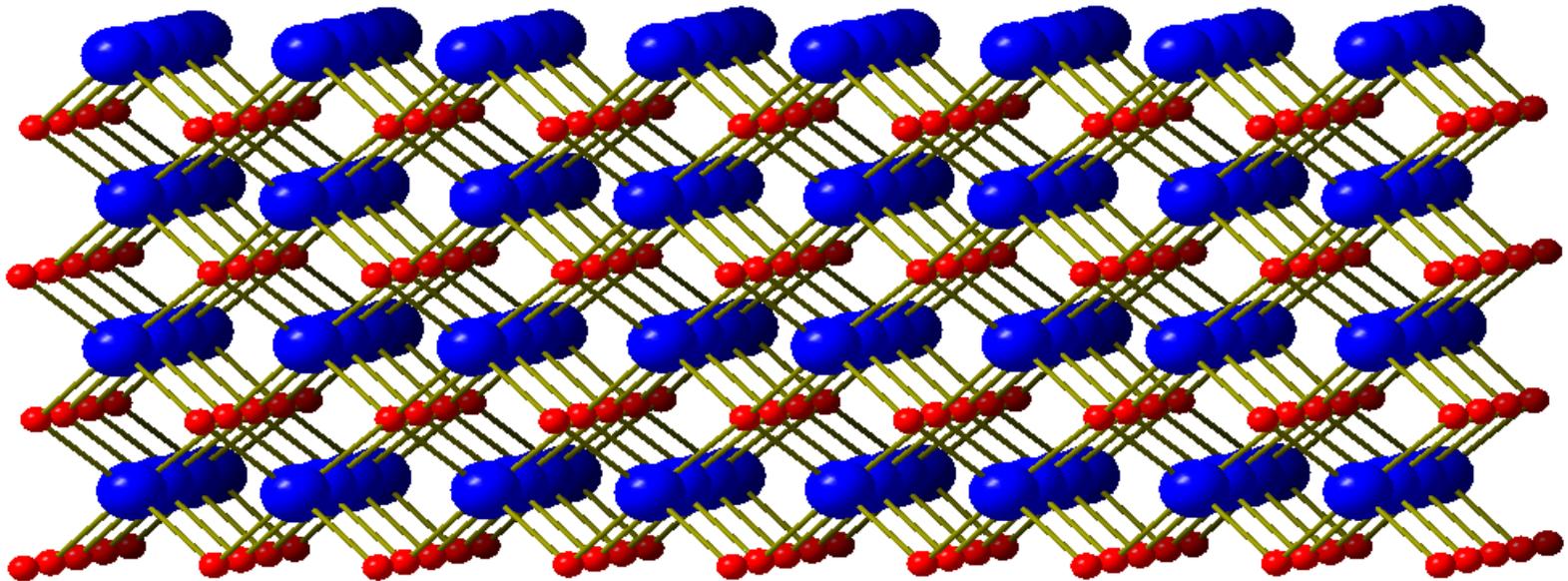
# How do we create Bandgap Engineered Structures? Epitaxy

- Repeating a crystalline structure by the atom by atom addition.
- Chemistry controls the epitaxy to insure that, for example, Ga bonds only to N and not Ga-Ga or N-N bonds\*.

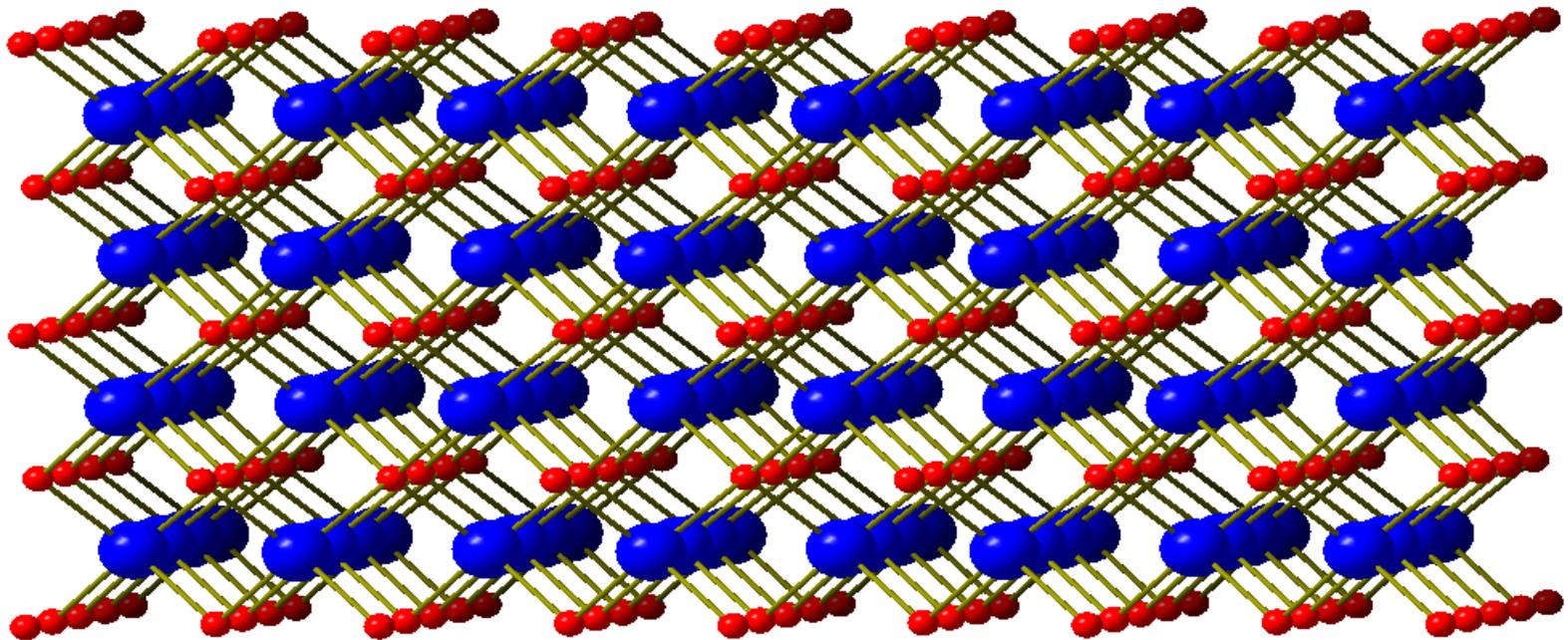


\*A small number of “antisite” defects (Ga-Ga or N-N bonds) actually do form but are typically in the parts per trillion concentration.

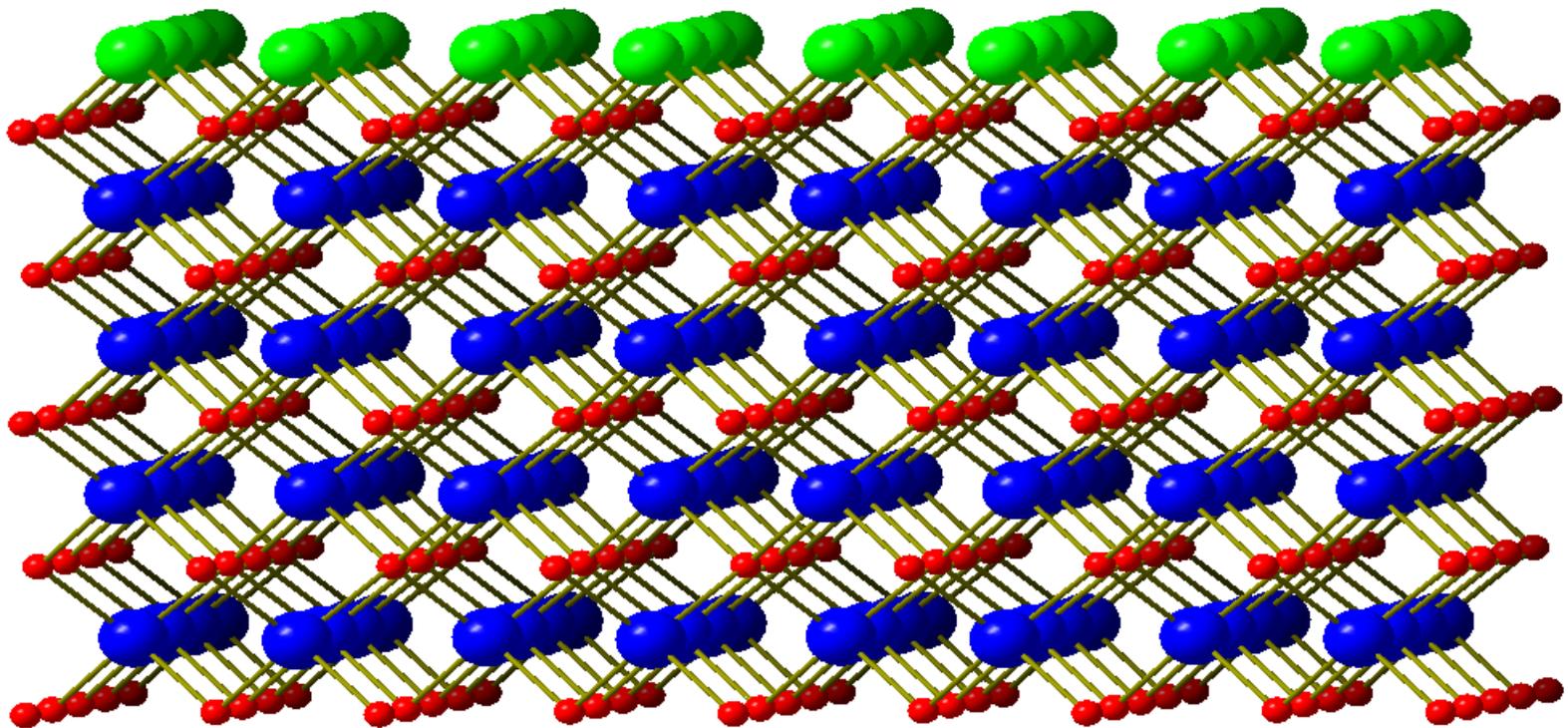
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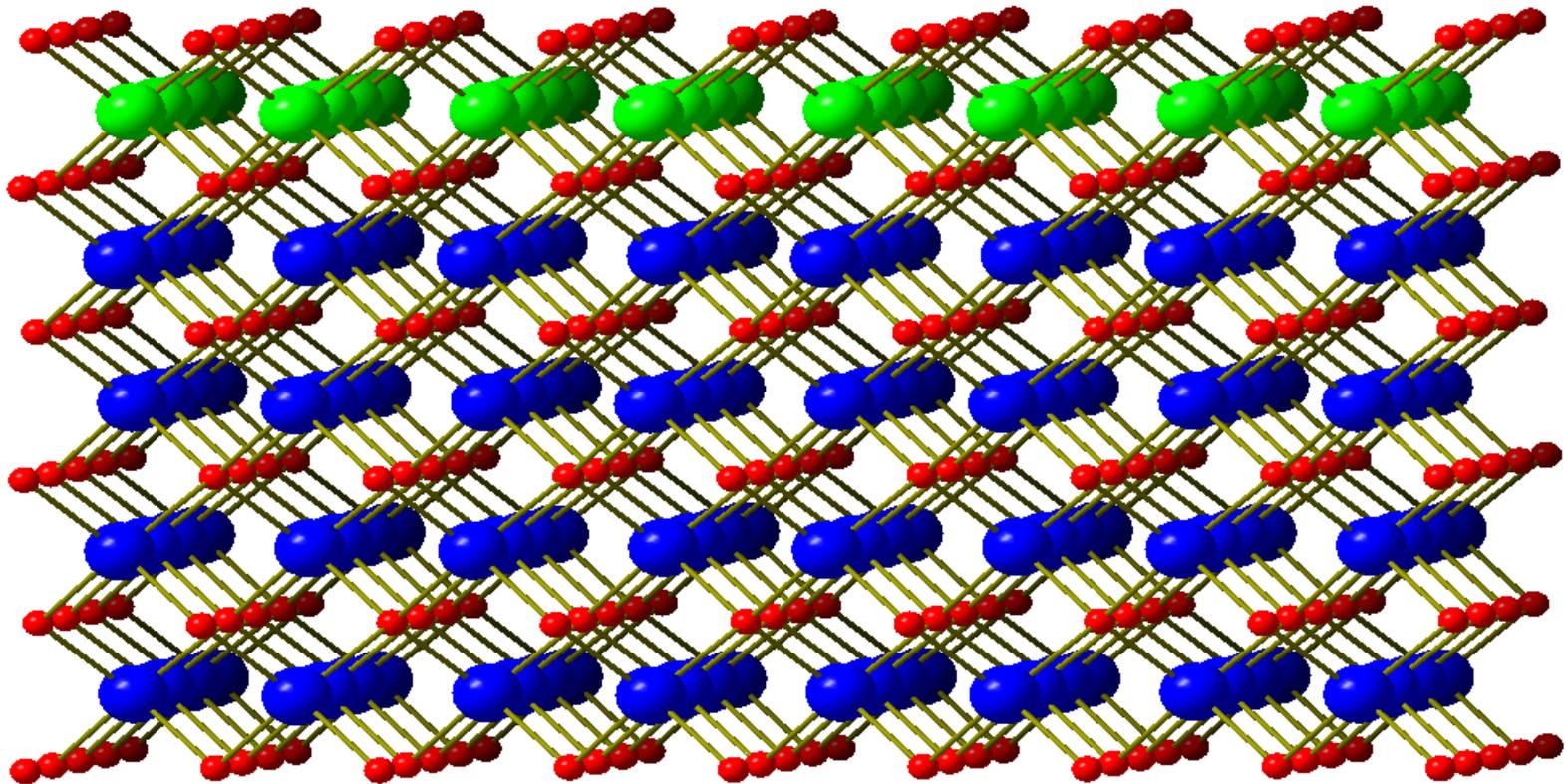
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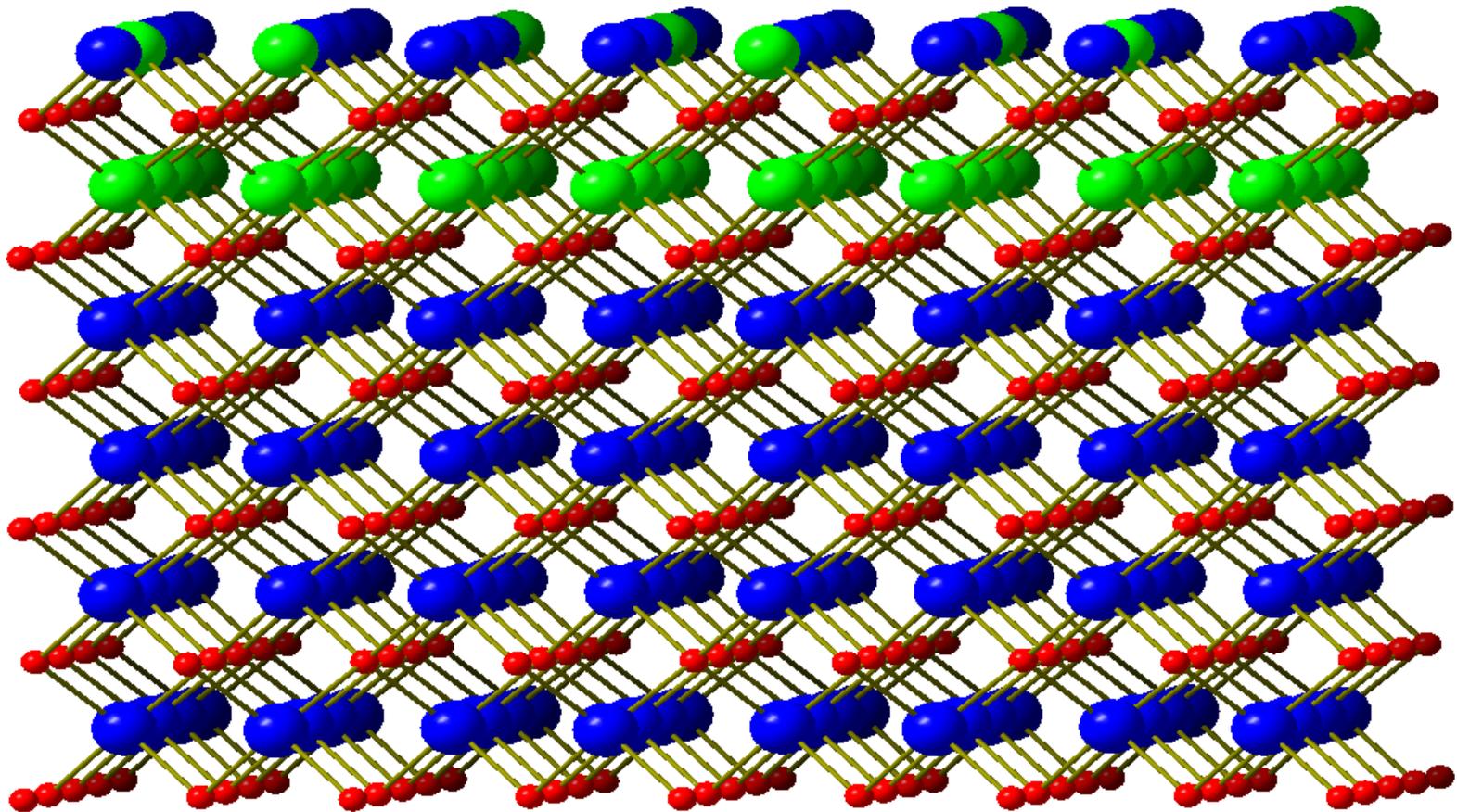
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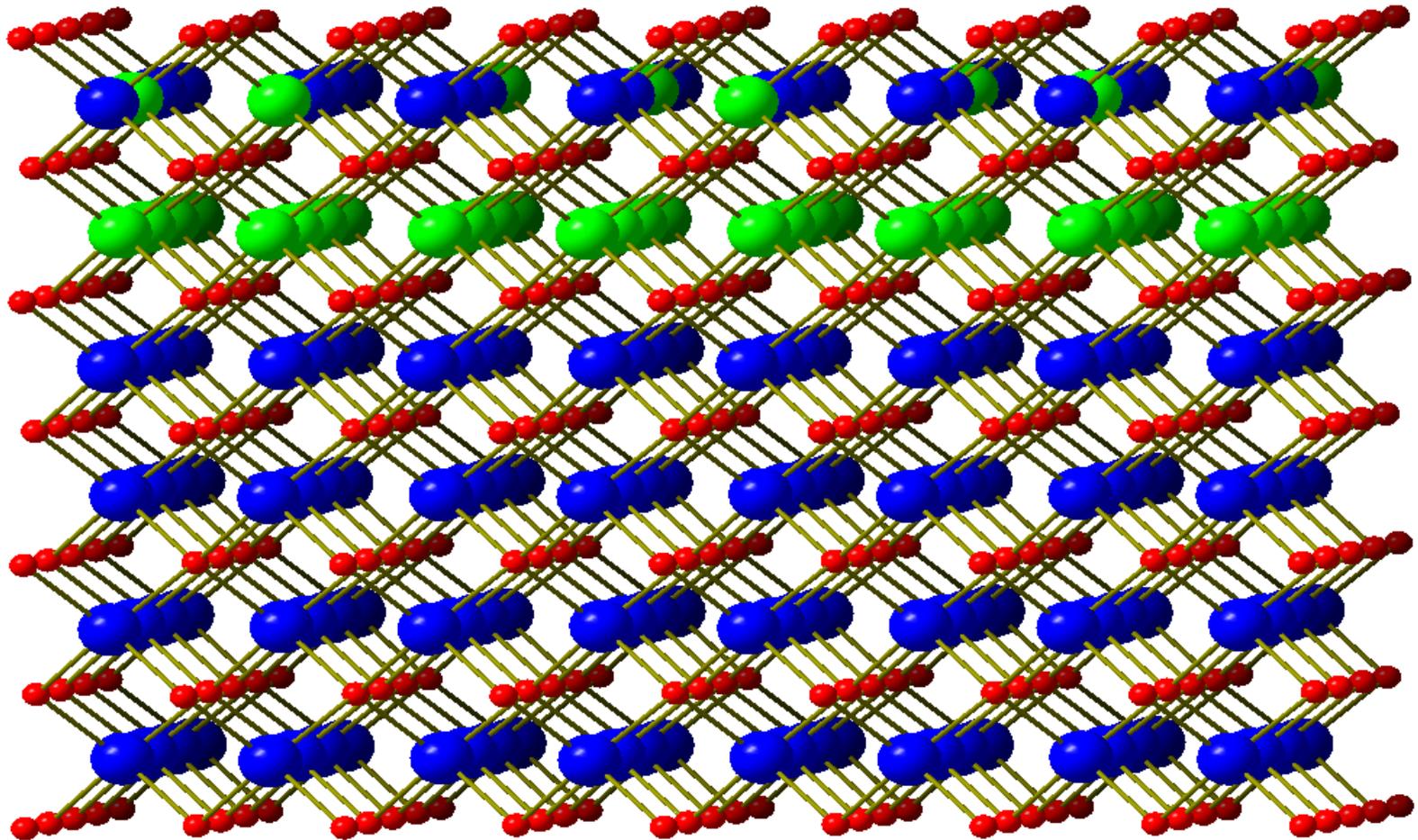
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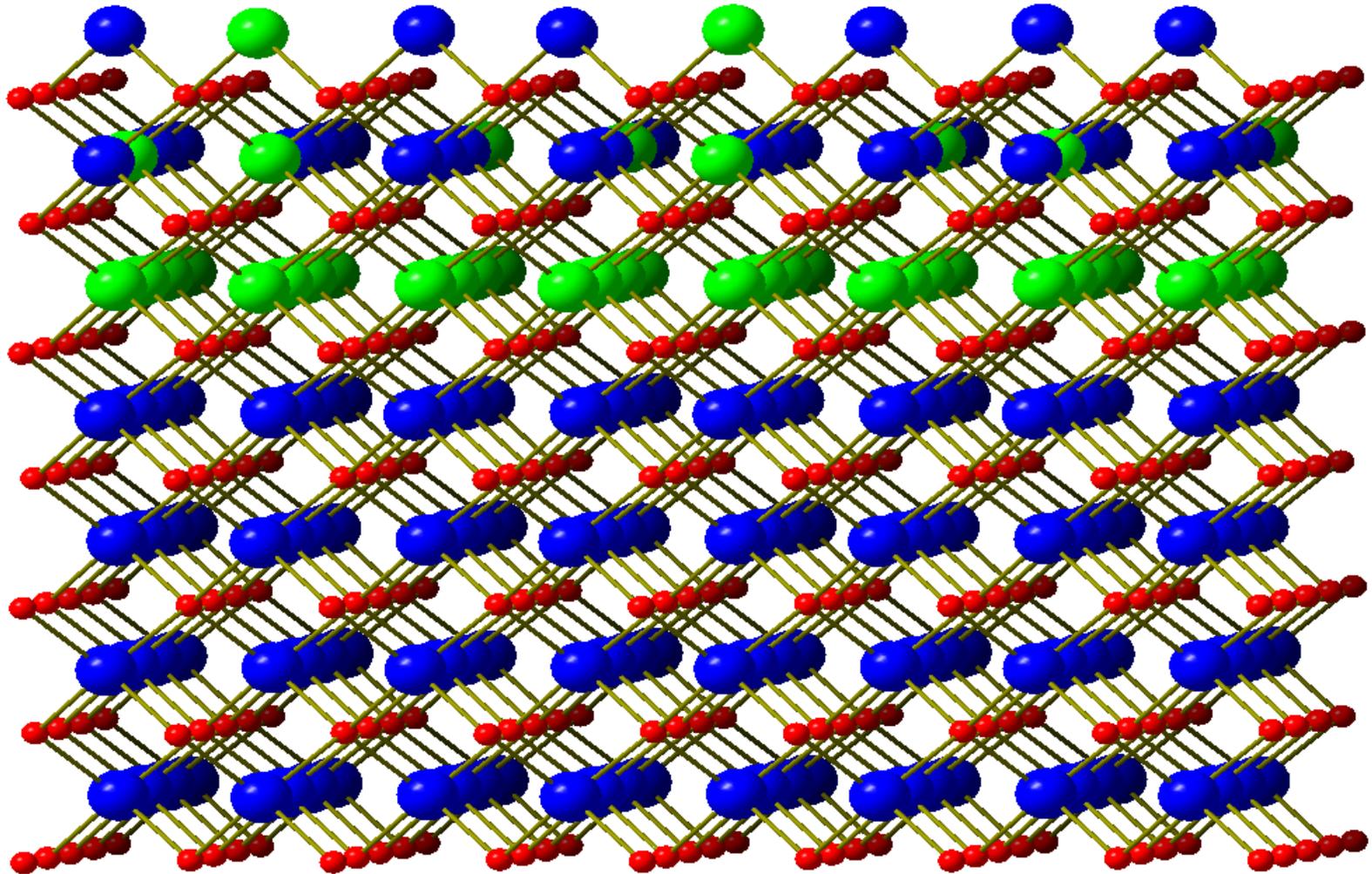
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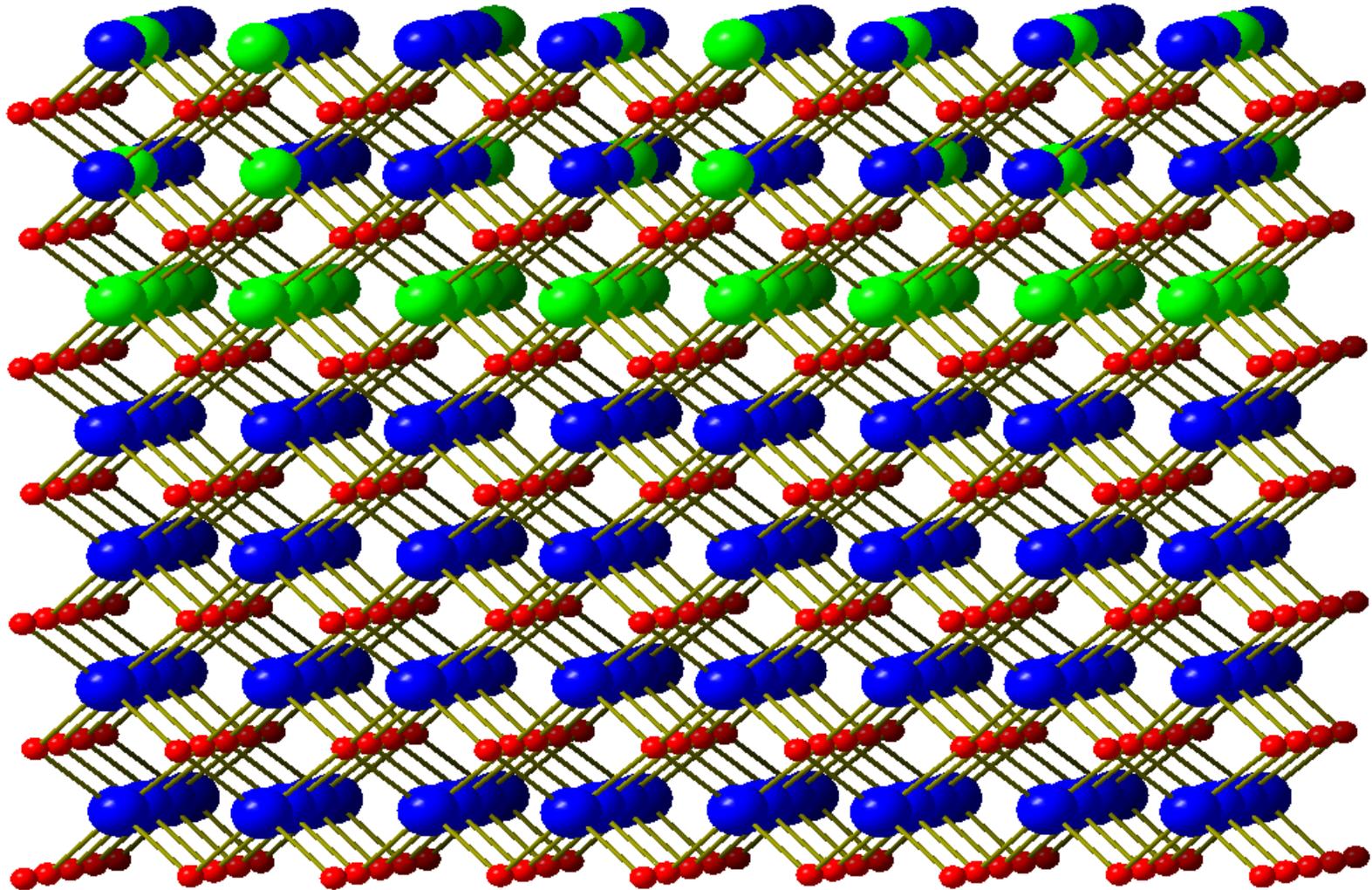
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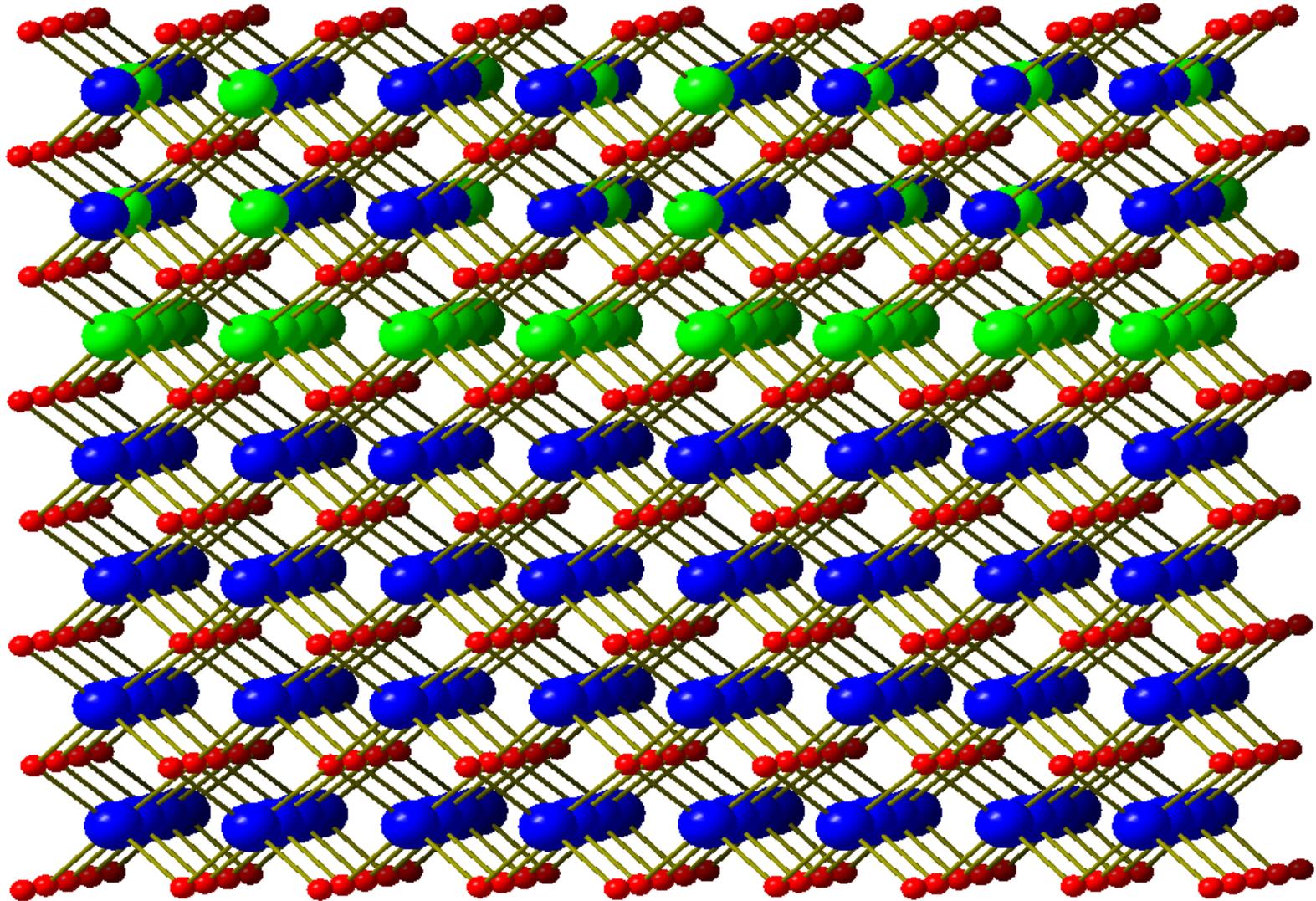
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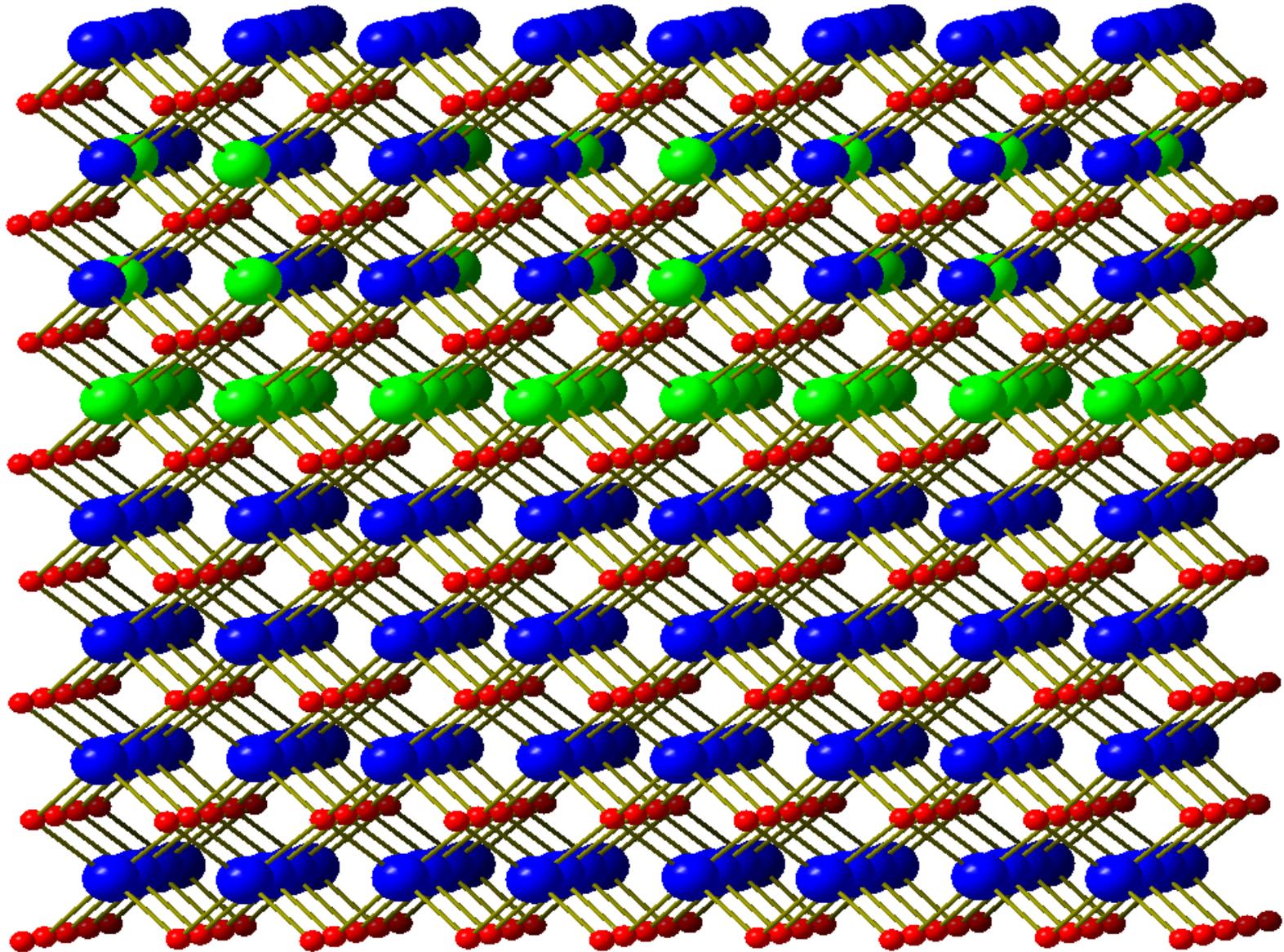
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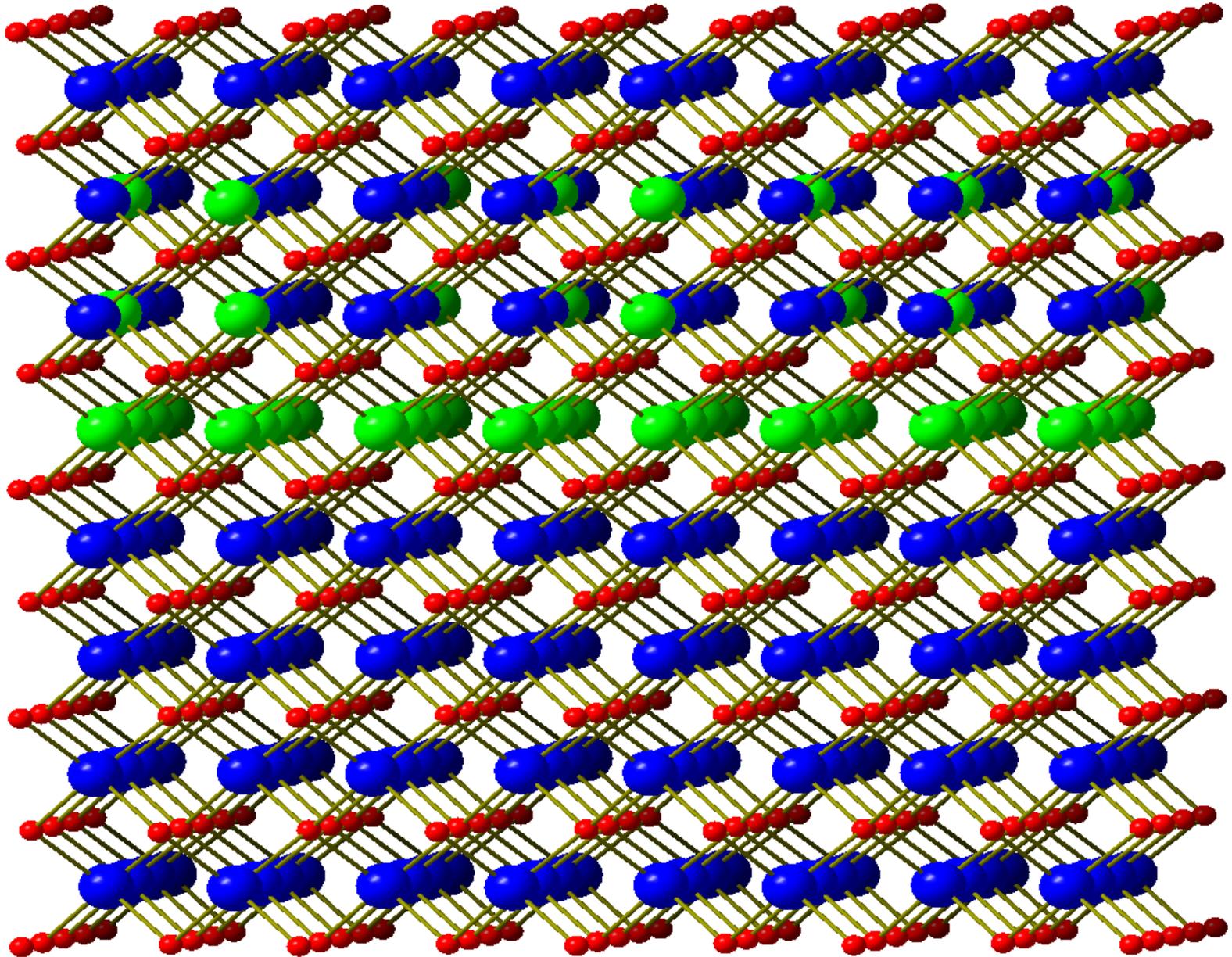
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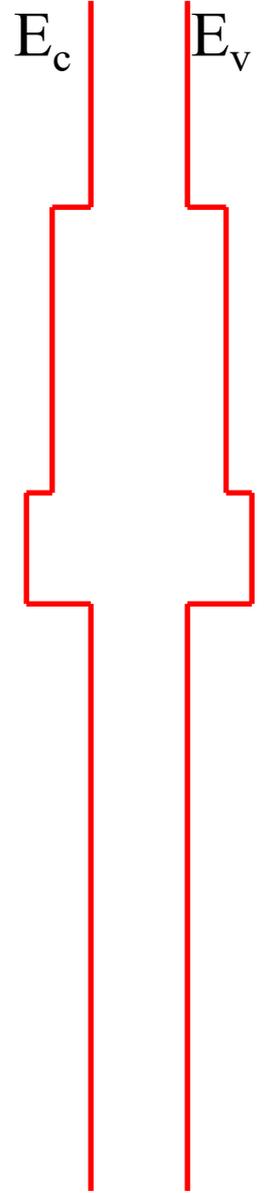
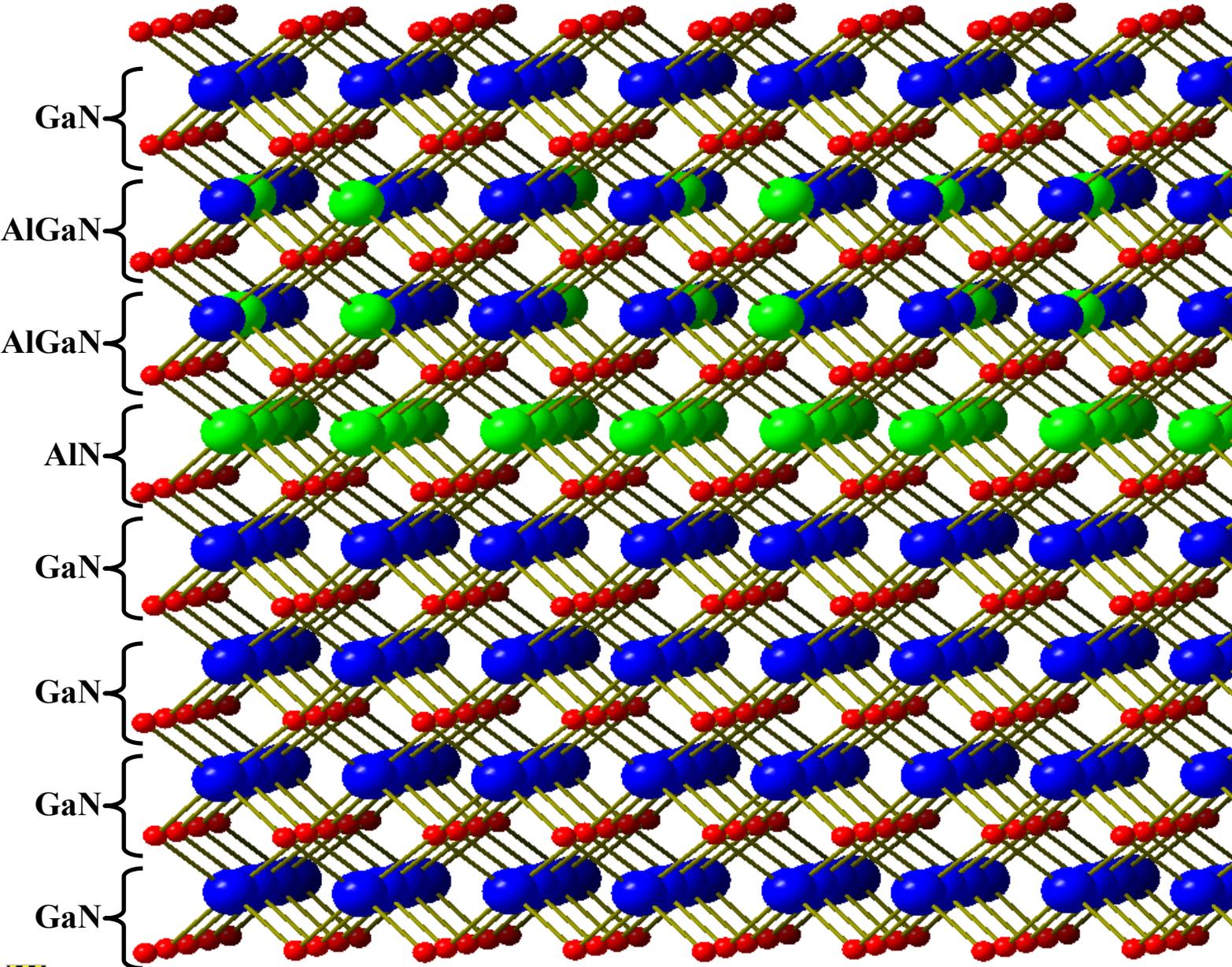
# How do we create Bandgap Engineered Structures? Epitaxy



# How do we create Bandgap Engineered Structures? Epitaxy



# How do we create Bandgap Engineered Structures? Epitaxy



# Engineered Energy Behavior in Compound Semiconductors

The potential distributions we will use in this class are all possible/common in device structures. Some may represent “grown in potentials” (quantum wells, etc..) or naturally occurring potentials (parabolic potentials often occur in nature – lattice vibrations for example) including periodic potentials such as lattice atoms.

