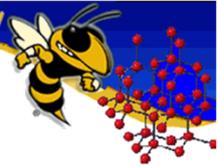


# Lecture 1

## Introduction to Electronic Materials

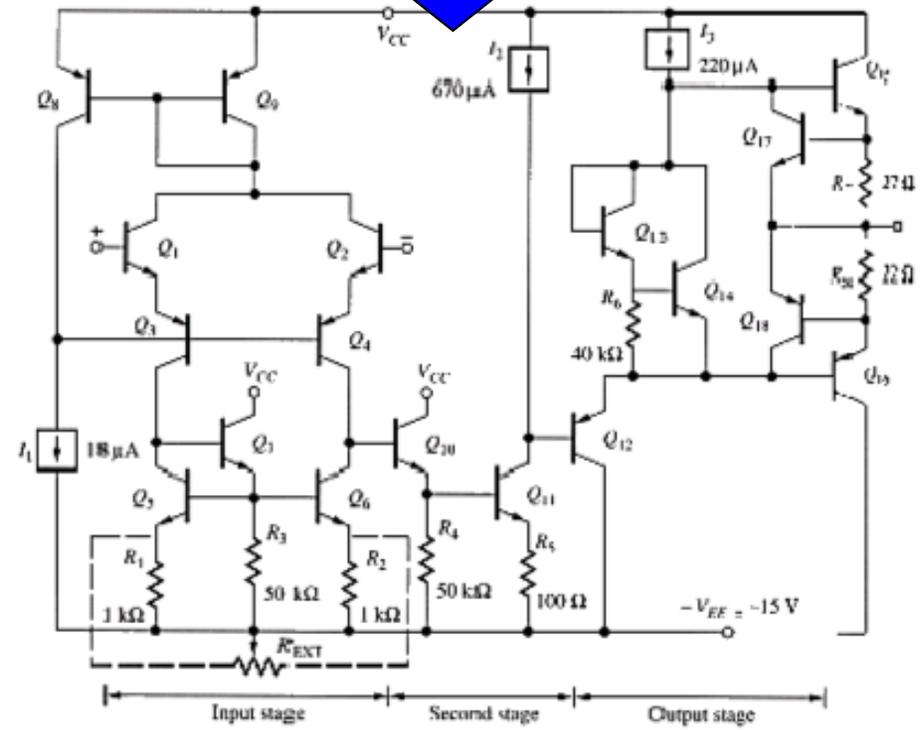
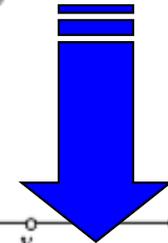
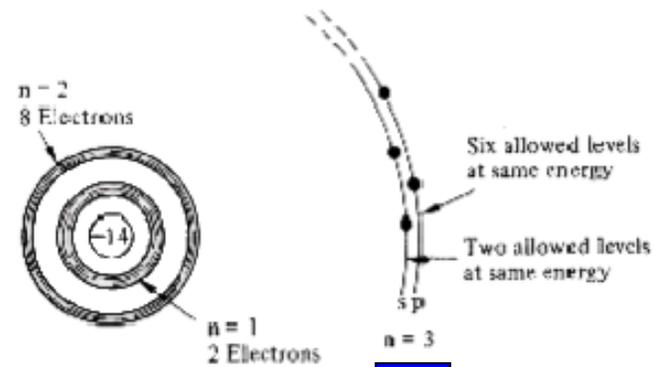
**Reading:**

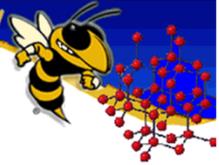
**Pierret 1.1, 1.2, 1.4, 2.1-2.6**



# Atoms to Operational Amplifiers

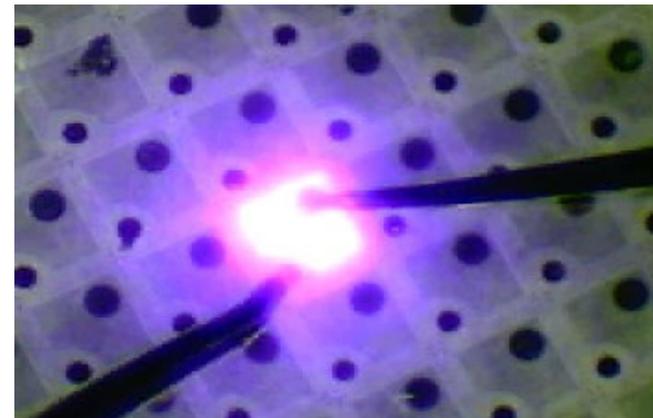
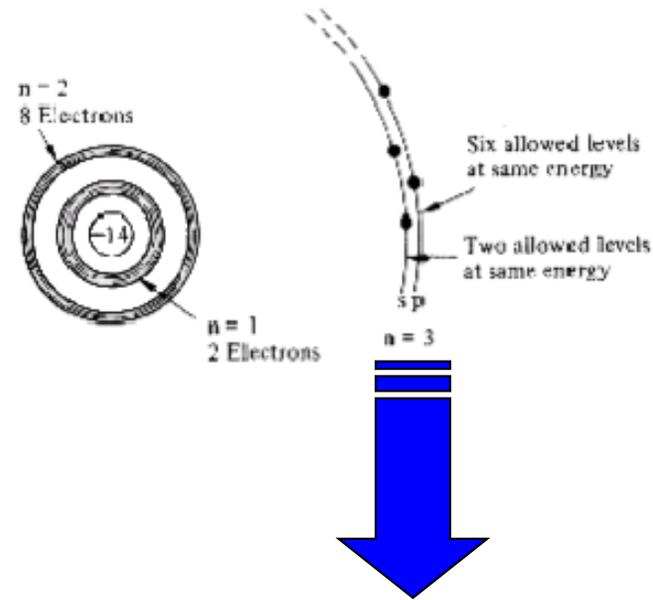
- The goal of this course is to teach the fundamentals of non-linear circuit elements including diodes, and transistors (BJT and FET), how they are used in circuits and real world applications.
- The course takes an “atoms to op-amps” approach in which you learn about the fundamentals of electron movement in semiconductor materials and develop this basic knowledge into how we can construct devices from these materials that can control the flow of electrons in useful ways.
- We then extend this knowledge to how these devices can be used to form circuits that perform useful functions on electrical signals.



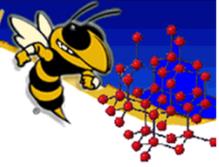


# ... Atoms to Everything Else in Optoelectronics

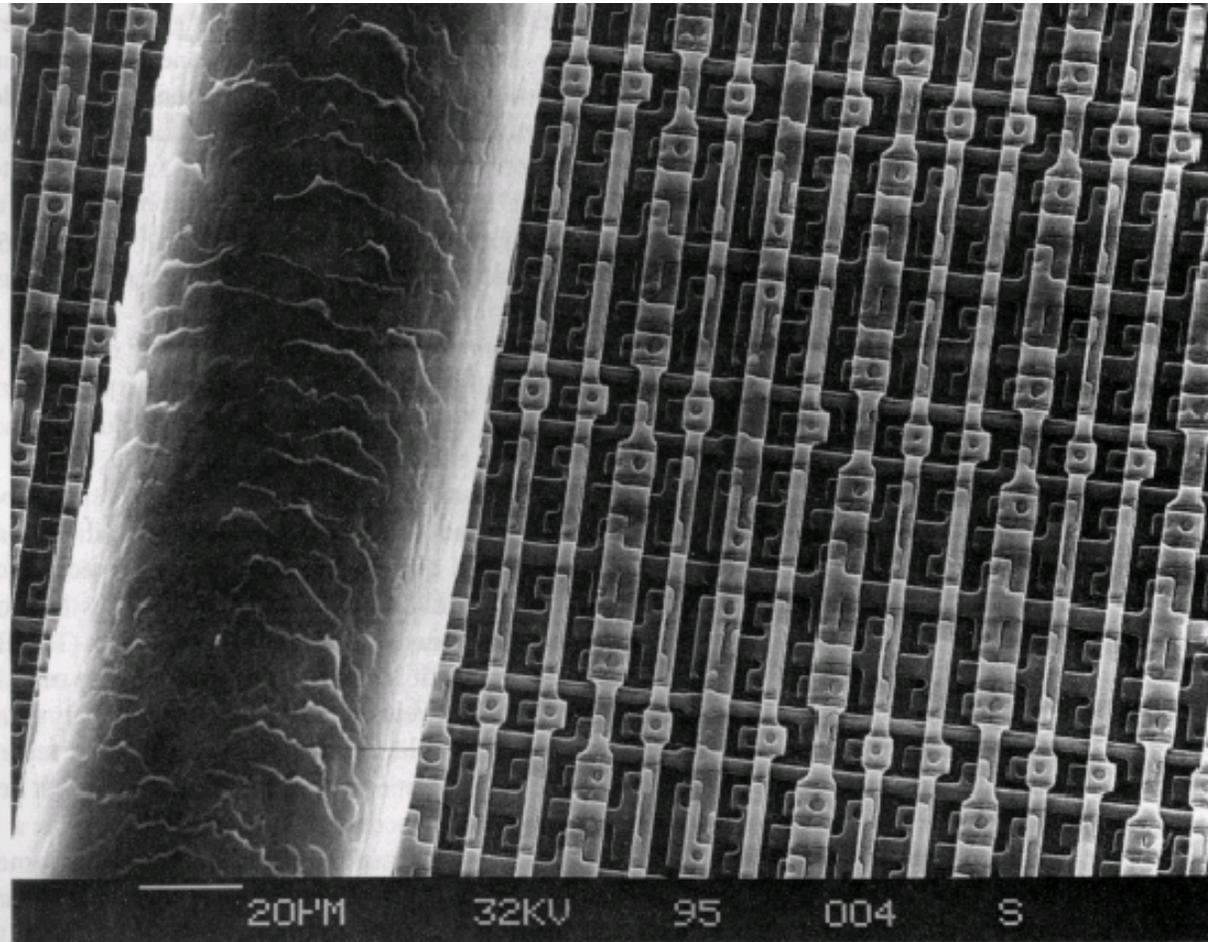
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- We then extend this knowledge to how these devices can be used to form circuits that perform useful functions on electrical signals.



Nakamura, S. *et al.*, “High-power InGaN single-quantum-well-structure blue and violet light-emitting diodes,” *Appl. Phys. Lett* **67**, 1868 (1995).



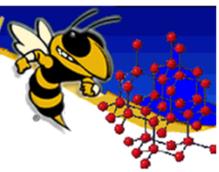
# Modern amplifiers consist of extremely small devices



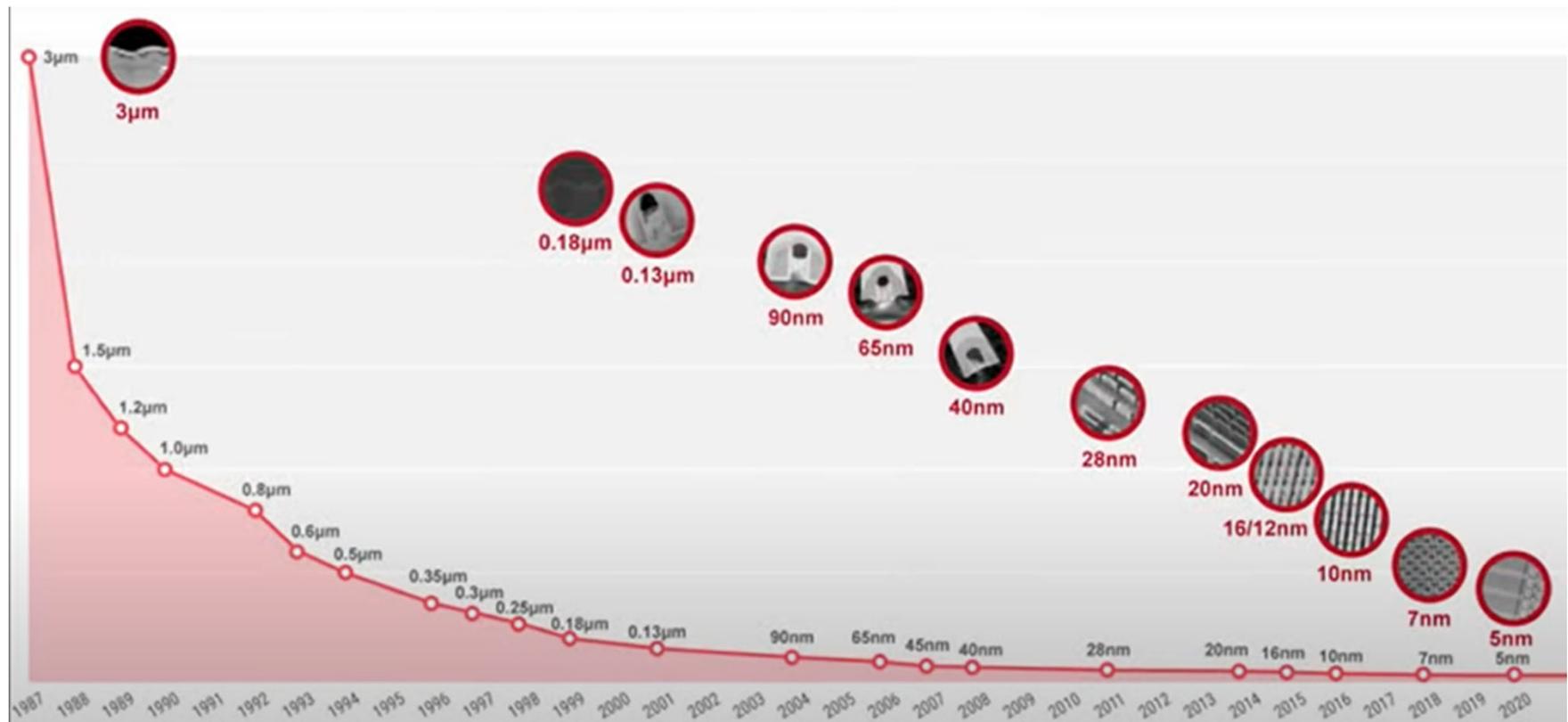
**Figure 1-2** Scanning electron micrograph (SEM) of an IC circa mid 1980s. The visible lines correspond to metal wires connecting the transistors.

Transistors in the above image are only a few microns ( $\mu\text{m}$  or  $1\text{e-}6$  meters) on a side.

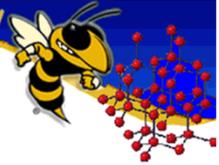
Modern devices have lateral dimensions that are only fractions of a micron ( $\sim 0.01 \mu\text{m}$ ) and vertical dimensions that may be only a few atoms tall.



# Modern amplifiers consist of extremely small devices

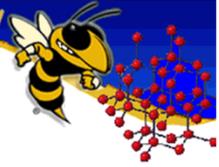


Modern devices have lateral dimensions that are only fractions of a micron ( $\sim 0.01 \mu\text{m}$ ) and vertical dimensions that may be only a few atoms tall.

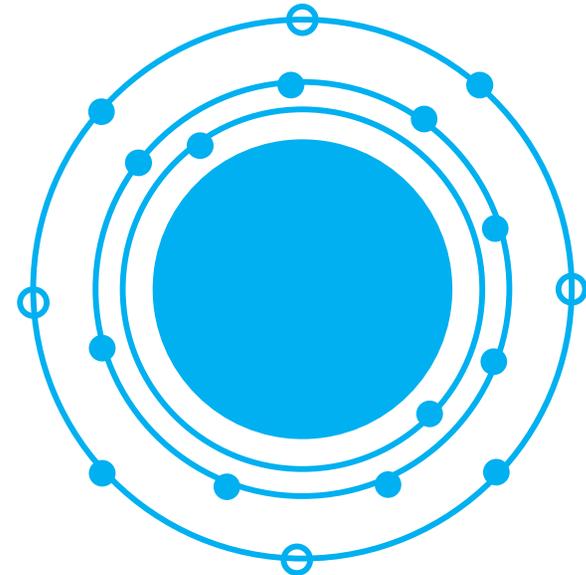
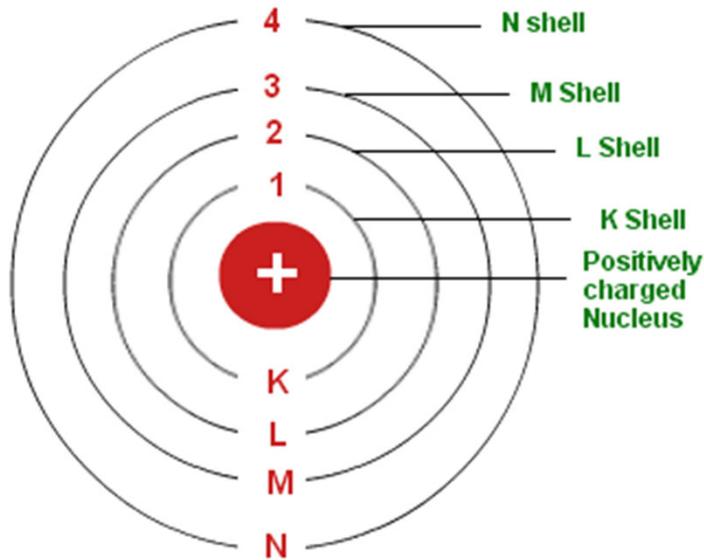


# Control of Conductivity is the Key to Modern Electronic Devices

- Conductivity,  $\sigma$ , is the ease with which a given material conducts electricity.
- Ohms Law:  $V=IR$  or  $J=\sigma E$  where  $J$  is current density and  $E$  is electric field.
  - Metals: High conductivity
  - Insulators: Low Conductivity
  - Semiconductors: Conductivity can be varied by several orders of magnitude.
- It is the ability to control conductivity that make semiconductors useful as “current/voltage control elements”. “Current/Voltage control” is the key to switches (digital logic including microprocessors etc...), amplifiers, LEDs, LASERs, photodetectors, etc...

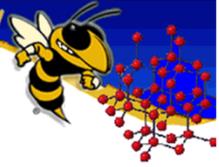


# Classifications of Electronic Materials



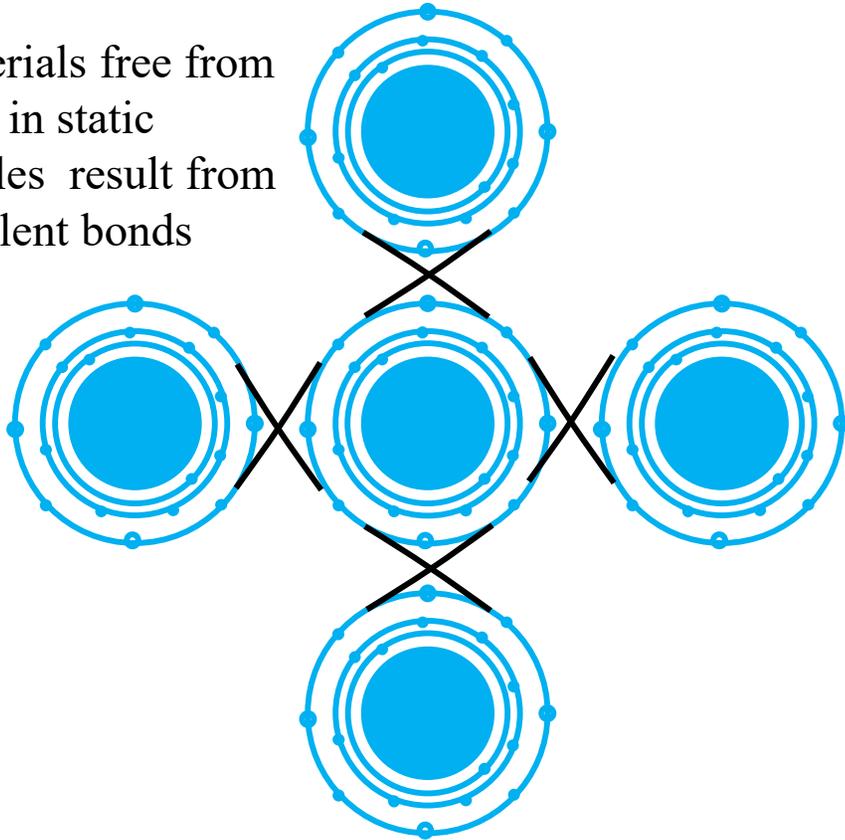
Example: Silicon  $n=1$  (2 s),  $n=2$  (2 s and 6 p) and  $n=3$  (2 s and 2 p with 4 unoccupied p states)

- Atoms contain various “orbitals”, “levels” or “shells” of electrons labeled as  $n=1, 2, 3, 4$ , 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.

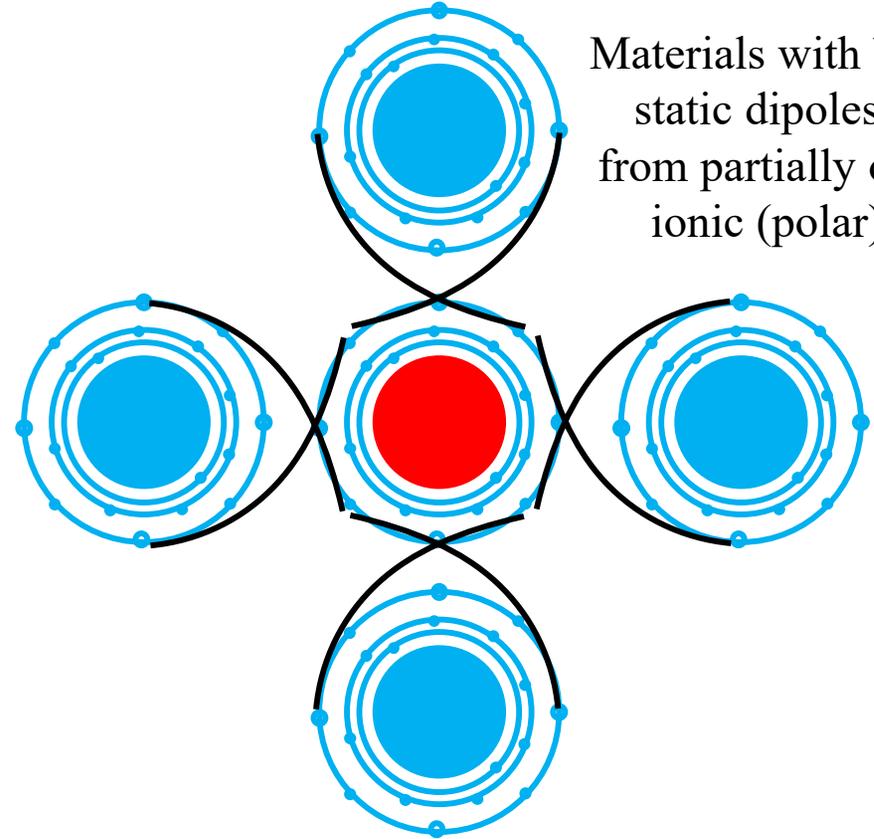


# Classifications of Electronic Materials

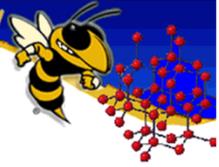
Materials free from built in static dipoles result from covalent bonds



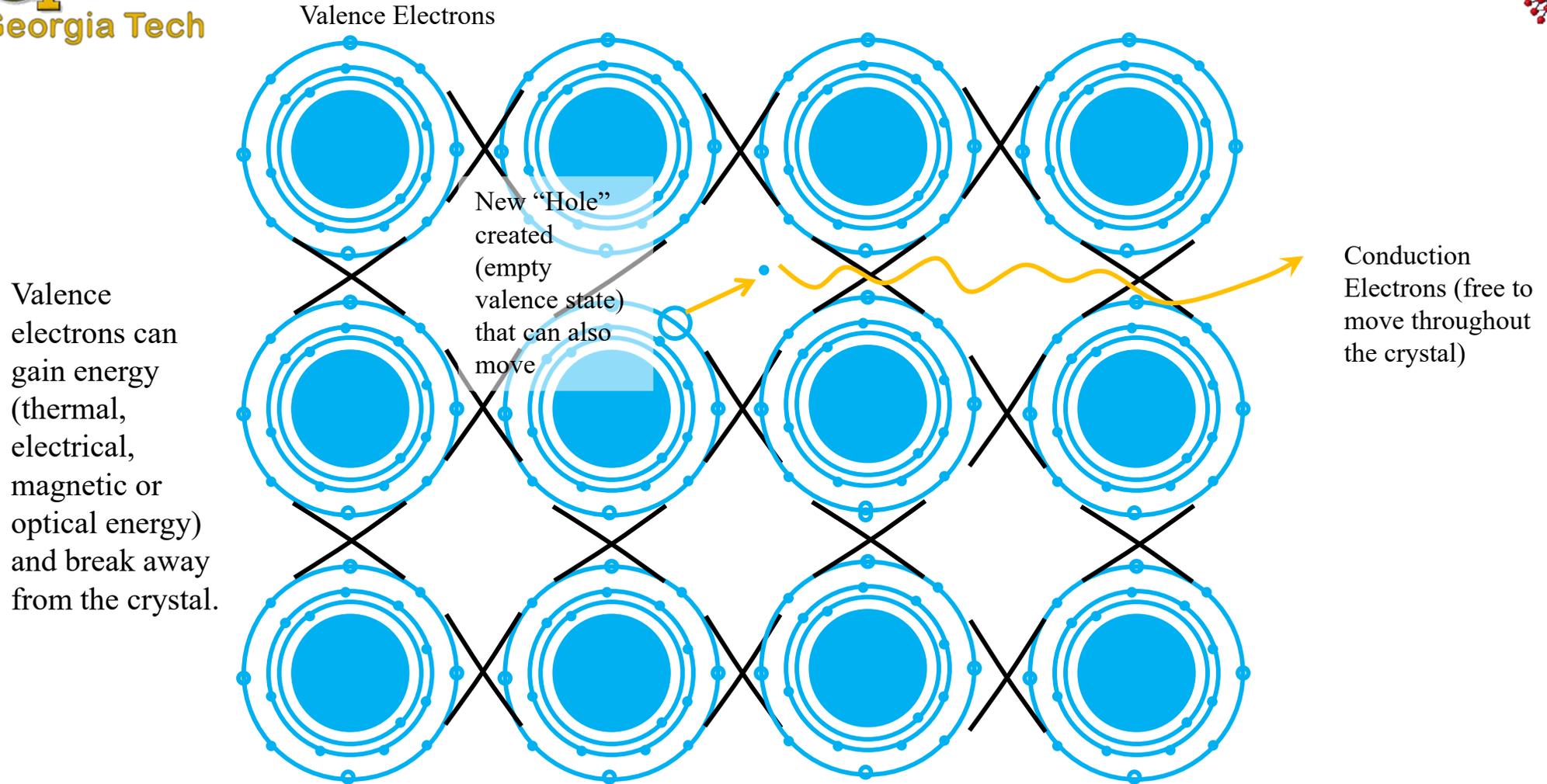
Materials with built in static dipoles result from partially or fully ionic (polar) bonds



- 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.

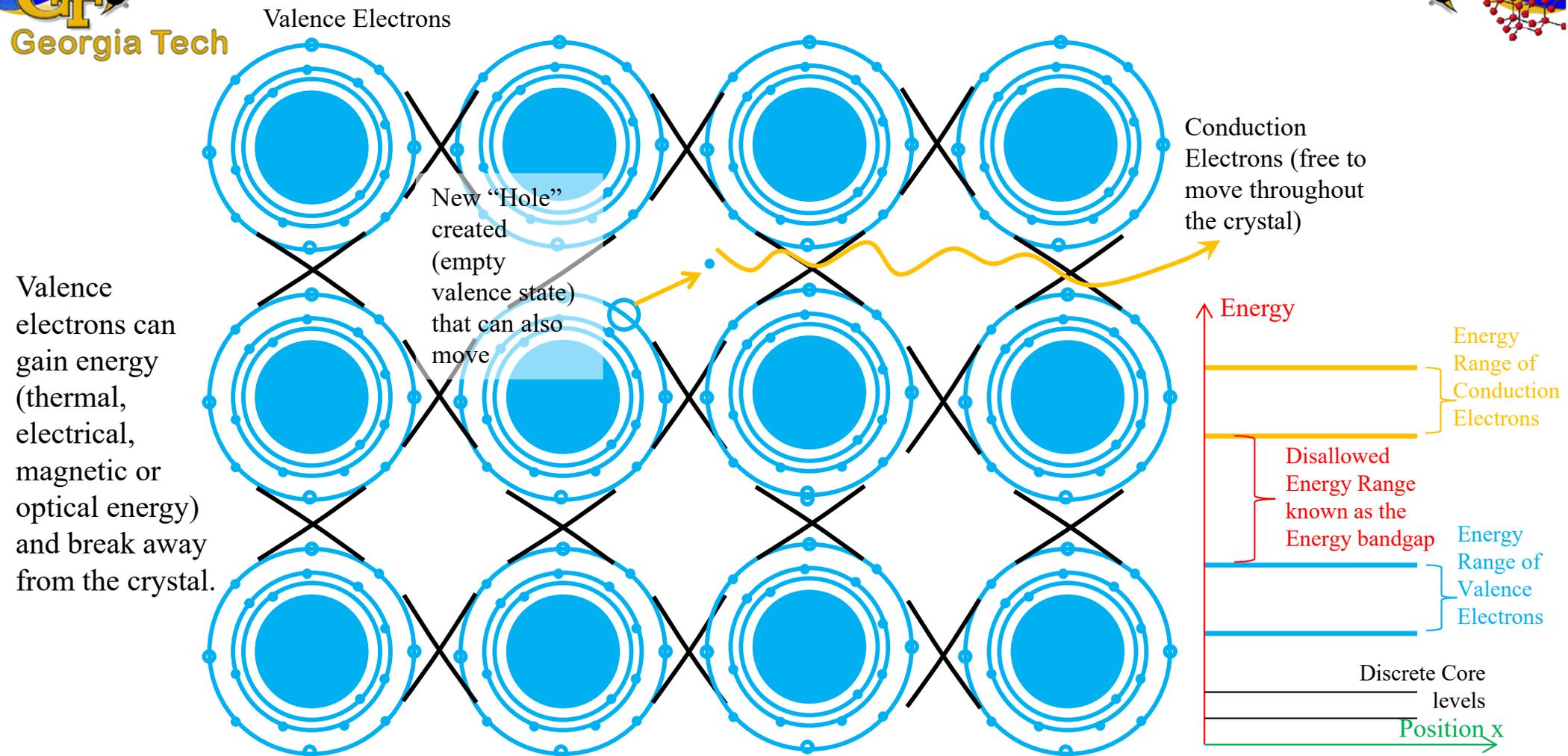
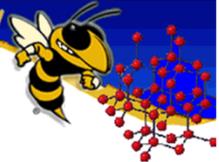


# Classifications of Electronic Materials



- 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

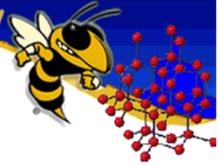


• Since the electrons in the valence orbitals of a solid can have a range of energies and since the free conducting electrons can have a range of energies, semiconductor materials are a sub-class of materials distinguished by the existence of a range of disallowed energies between the energies of the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

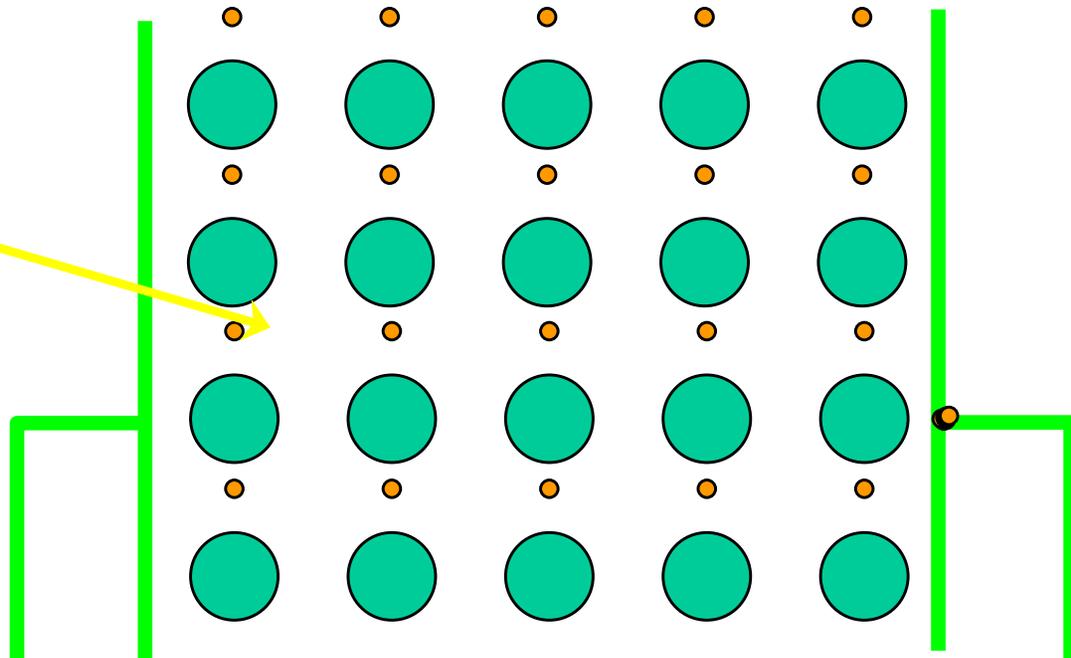
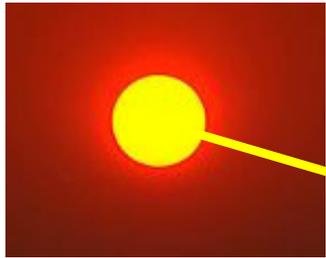
• The energy difference (**energy gap or bandgap**) between the states in which the electron is bound to the atom and when it is free to conduct throughout the crystal is related to the bonding strength of the material, its density, the degree of ionicity of the bond, and the chemistry related to the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

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

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



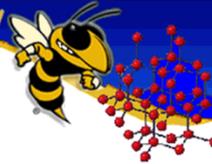
# Example: Solar Cells



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



•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.

•One question that repeatedly comes up: Why does the bandgap form instead of just s and p orbital mixing? While complex beyond this explanation, the answer is in the way the s and p orbitals “hybridize” (mix). As the mixing becomes “severe”, they must separate more fully, leaving a range of energies where no electron can exist – the energy bandgap.

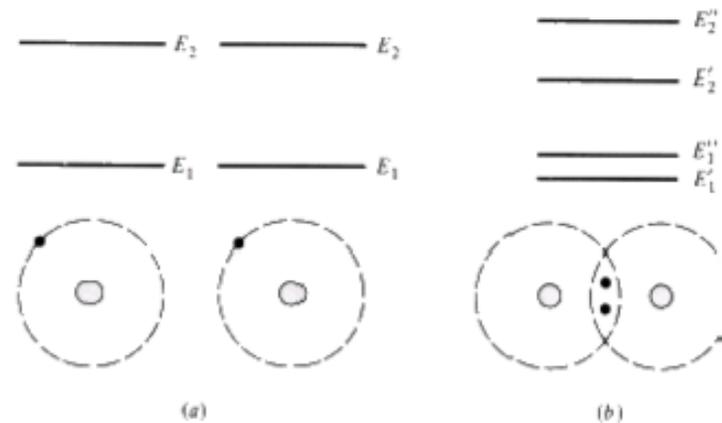
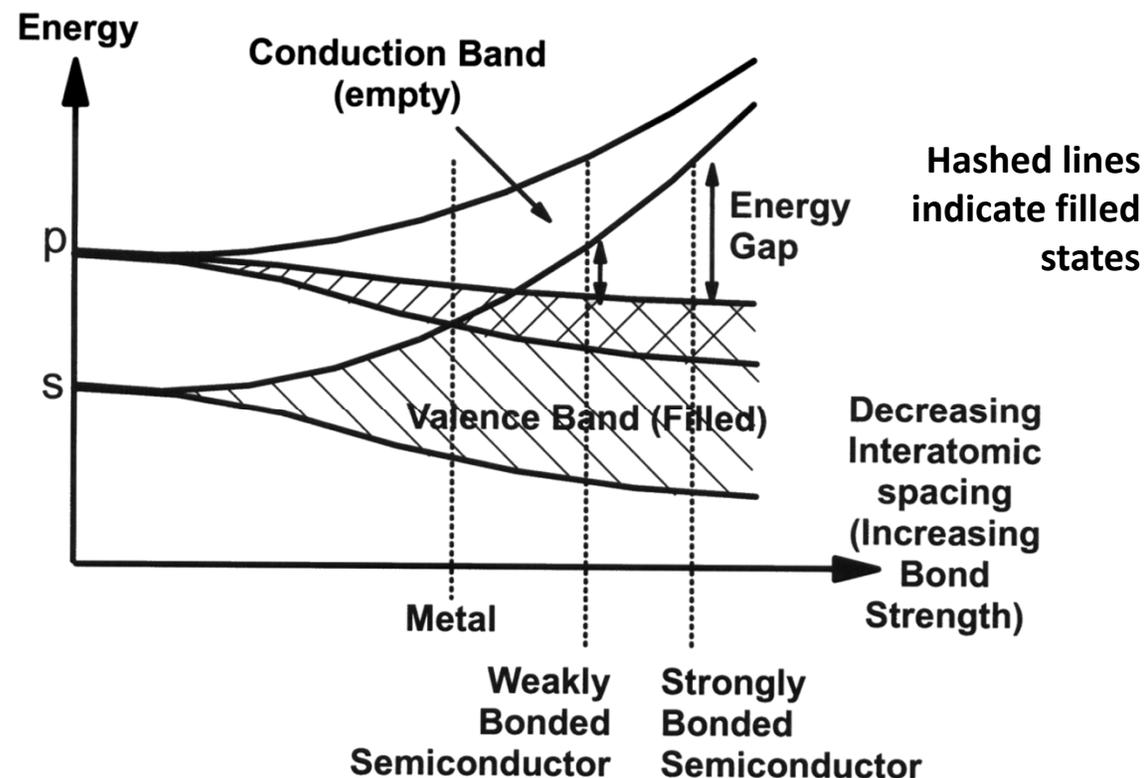
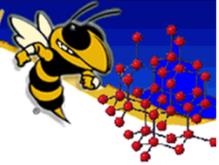


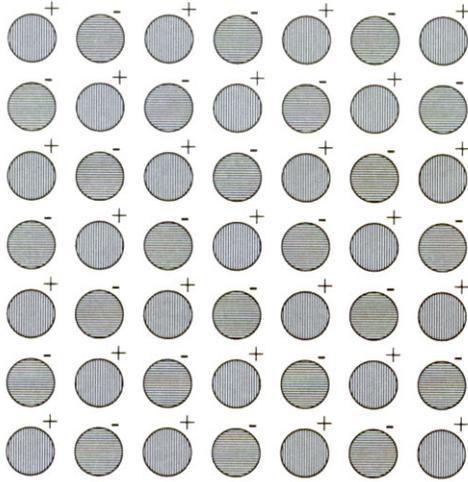
FIGURE 1-9 Two hydrogen atoms: (a) non-interacting and (b) interacting. Splitting of energy levels is illustrated for (b).



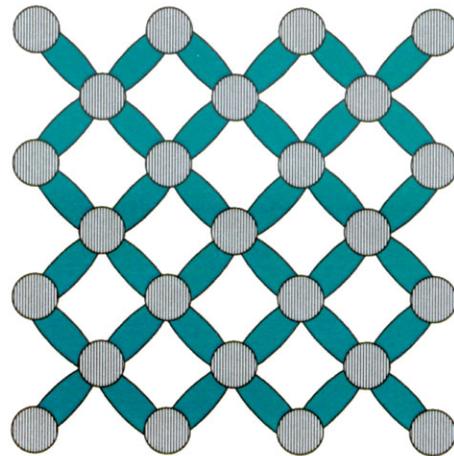


# Material Classifications based on Bonding Method

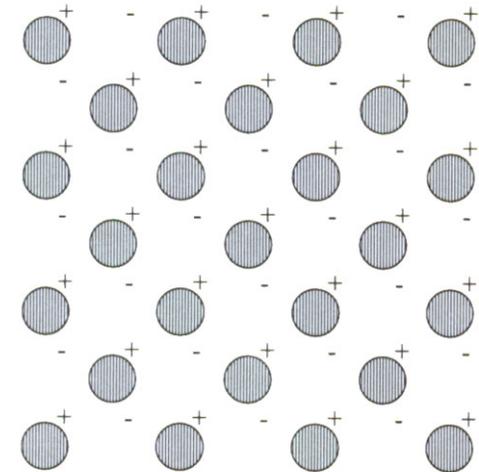
Bonds can be classified as metallic, Ionic, Covalent, and van der Waals.



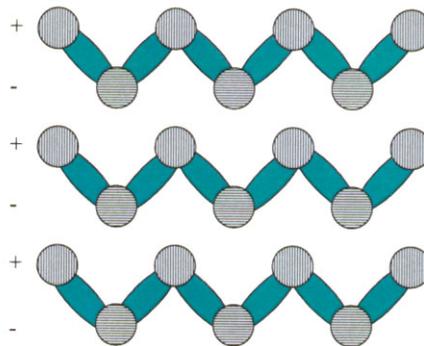
**Ionic Bonding:** One atom acquires and holds the electron(s) of an adjacent atom. Bonding is coulombic and strong.



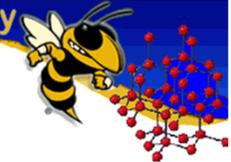
**Covalent Bonding:** Atoms share electrons with the surrounding atoms. Bonding is moderately weak.



**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	$\sim 0.08$ eV*
Pb	1.81/** Angstroms	Metal

## ELEMENTS

Selected Radioactive Isotopes

Naturally occurring radioactive isotopes are designated by a mass number in blue (although some are also manufactured). Letter in italics indicates an isomer of another isotope of the same mass number. Half-lives follow in parentheses, where s, min, h, d, and y stand respectively for seconds, minutes, hours, days, and years. The table includes mainly the longer-lived radioactive isotopes; many others have been prepared. Isotopes known to be radioactive but with half-lives exceeding  $10^{17}$  y have not been 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

IIB		IVB		VIB		VIIB		VIIIB		VIII	
										2	
										4.00260	
										4.215	
										0.1787	
										He	
										1s <sup>2</sup>	
										He	
										Ne	
										Ne	
										Ar	
										Ar	
										Kr	
										Kr	
										Xe	
										Xe	
										Rn	
										Rn	

37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	89	104	105	106												
Fr	Ra	Ac	Unq	Unp	Unh												

\* Only has a measurable bandgap near 0K

\*\* Different bonding/Crystal Structure due to unfilled higher orbital states

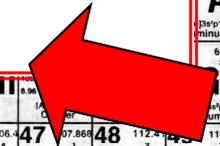
58	59	60	61	62	63	64	65	66	67	68	69	70	71	72
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
90	91	92	93	94	95	96	97	98	99	100	101	102	103	
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

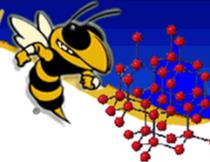
KEY: ATOMIC NUMBER, ATOMIC WEIGHT (2), BOILING POINT, K, MELTING POINT, K, DENSITY at 300 K (3) (g/cm<sup>3</sup>), ELECTRON CONFIGURATION, NAME.

NOTES: (1) Black — solid, Red — gas, Blue — liquid, Outline — synthetically prepared.

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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

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.

## PERIODIC TABLE OF THE ELEMENTS

Table of Selected Radioactive Isotopes

GROUP	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA	IB	IIB	IIIB	IVB	VB	VIB	VIIA	VIII																																																						
1	1.0079 H Hydrogen	4	9.01218 He Helium													2 4.00260 He Helium																																																						
2	20.206 Li Lithium	3	6.941 Be Beryllium														8 12.011 C Carbon																																																					
3	453.7 Na Sodium	11 22.98977 Mg Magnesium	12 24.305 Al Aluminum	13 26.98154 Si Silicon	14 28.0855 P Phosphorus	15 30.97376 S Sulfur	16 32.06 Cl Chlorine	17 35.453 Ar Argon	18 39.948 K Potassium	19 39.0983 Ca Calcium	20 40.078 Sc Scandium	21 44.9559 Ti Titanium	22 47.88 V Vanadium	23 50.9415 Cr Chromium	24 51.9961 Mn Manganese	25 54.938 Fe Iron	26 55.845 Co Cobalt	27 58.9332 Ni Nickel	28 58.707 Cu Copper	29 63.546 Zn Zinc	30 65.38 Ga Gallium	31 69.723 Ge Germanium	32 72.59 As Arsenic	33 74.9216 Se Selenium	34 78.96 Br Bromine	35 79.904 Kr Krypton	36 83.80 Rb Rubidium	37 85.4678 Sr Strontium	38 87.62 Y Yttrium	39 88.9059 Zr Zirconium	40 91.224 Nb Niobium	41 92.9063 Mo Molybdenum	42 95.94 Tc Technetium	43 98.9062 Ru Ruthenium	44 101.07 Rh Rhodium	45 101.07 Pd Palladium	46 106.42 Ag Silver	47 107.8682 Cd Cadmium	48 112.411 In Indium	49 114.818 Sn Tin	50 117.868 Sb Antimony	51 121.757 Te Tellurium	52 127.603 I Iodine	53 126.9054 Xe Xenon	54 131.30 Fr Francium	55 132.9054 Ra Radium	56 137.33 Ac Actinium	57 138.905 Th Thorium	58 174.97 Pa Protactinium	59 180.9479 U Uranium	60 183.85 Np Neptunium	61 186.207 Pu Plutonium	62 190.23 Am Americium	63 192.22 Cm Curium	64 195.08 Bk Berkelium	65 196.9665 Hf Hafnium	66 200.5 Ta Tantalum	67 204.37 W Tungsten	68 207.2 Re Rhenium	69 208.9804 Os Osmium	70 208.9804 Ir Iridium	71 208.9804 Pt Platinum	72 208.9804 Au Gold	73 208.9804 Hg Mercury	74 208.9804 Tl Thallium	75 208.9804 Pb Lead	76 208.9804 Bi Bismuth	77 208.9804 Po Polonium	78 208.9804 At Astatine	79 208.9804 Rn Radon

**KEY**

- ATOMIC NUMBER
- ATOMIC WEIGHT (2)
- OXIDATION STATES (Bold most stable)
- MELTING POINT, K
- BOILING POINT, K
- DENSITY at 300 K (g/cm<sup>3</sup>)
- ELECTRON CONFIGURATION
- NAME
- SYMBOL (1)

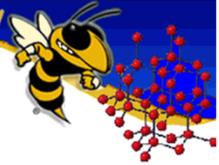
**NOTES:**

- (1) Black — solid, Red — gas, Blue — liquid.
- (2) Entries marked with asterisks refer to the gaseous state at 273 K and 1 atm and are given in units of g/l.
- (3) Entries marked with asterisks refer to the gaseous state at 273 K and 1 atm and are given in units of g/l.

† The names and symbols of elements 104 - 106 are those recommended by IUPAC as systematic alternatives to those suggested by the purported discoverers. Backus (USA) researchers have proposed Rutherfordium, Rf, for element 104 and Nichols (Mo, for element 105. Dubois (USFR) researchers, who also claim the discovery of these elements have proposed different names (and symbols).

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.

\* Estimated Values



# 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  $0 \leq x \leq 1$

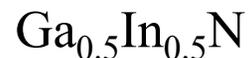
Quaternary:  $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$  where  $0 \leq x \leq 1$  and  $0 \leq y \leq 1$

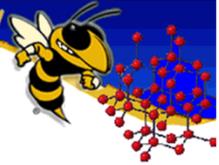
Half the total number of atoms must come from group III (Column III) and the other half the atoms must come from group V (Column V) (or more precisely, IV/IV, III/V, or II/VI combinations) leading to the above “reduced semiconductor notation that emphasizes the equal numbers of anion (higher valence electron group) and cations (lower valence electron group) in the compound.

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

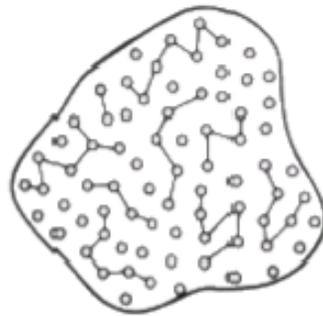


But the correct reduced semiconductor formula would be:

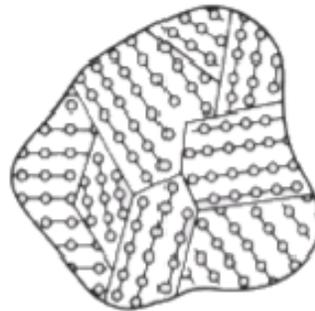




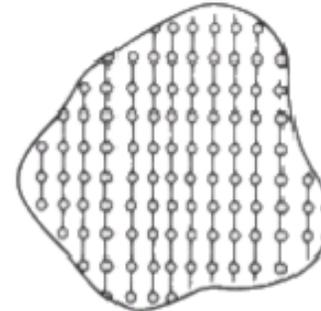
# Classifications of Electronic Materials



(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.

## Material Classifications based on Crystal Structure

### *Amorphous Materials*

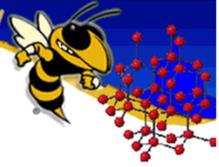
No discernible long range atomic order (no detectable crystal structure). Examples are silicon dioxide ( $\text{SiO}_2$ ), amorphous-Si, silicon nitride ( $\text{Si}_3\text{N}_4$ ), and others. Though usually thought of as less perfect than crystalline materials, this class of materials is extremely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

### *Polycrystalline Materials*

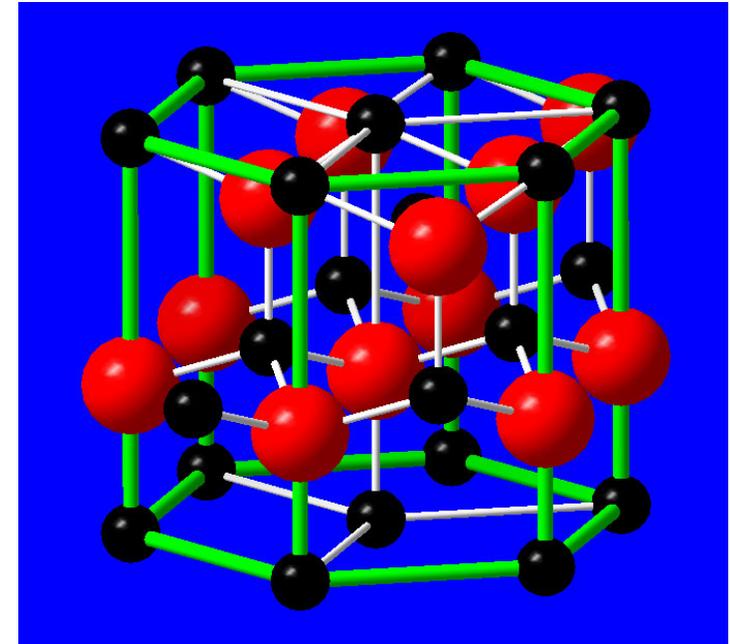
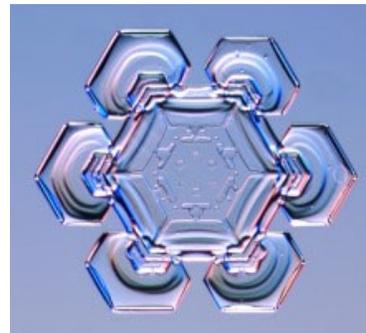
Material consisting of several “domains” of crystalline material. Each domain can be oriented differently than other domains. However, within a single domain, the material is crystalline. The size of the domains may range from cubic nanometers to several cubic centimeters. Many semiconductors are polycrystalline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



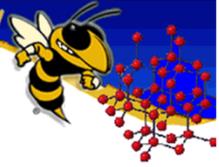
# Crystalline Order



Water Molecules,  $H_2O$ , forming “Snowflakes”

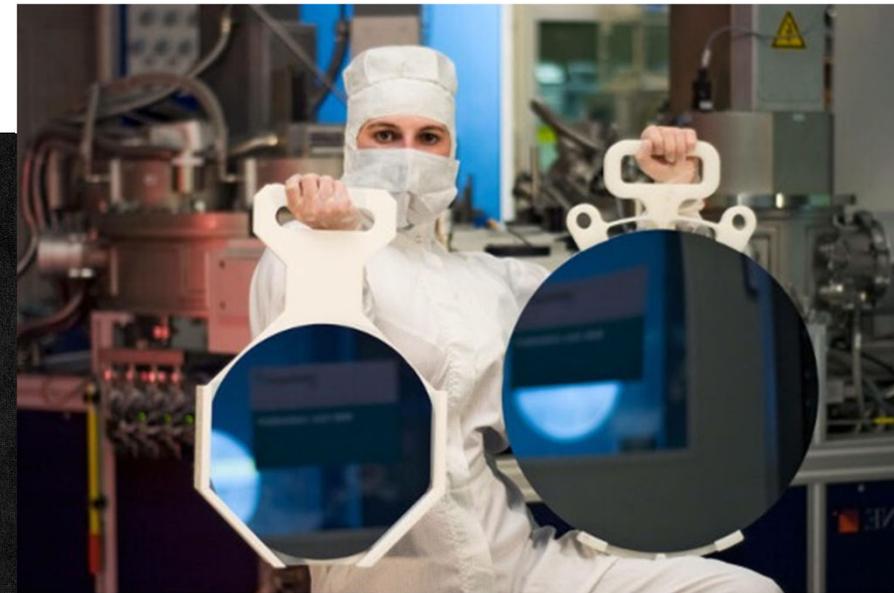
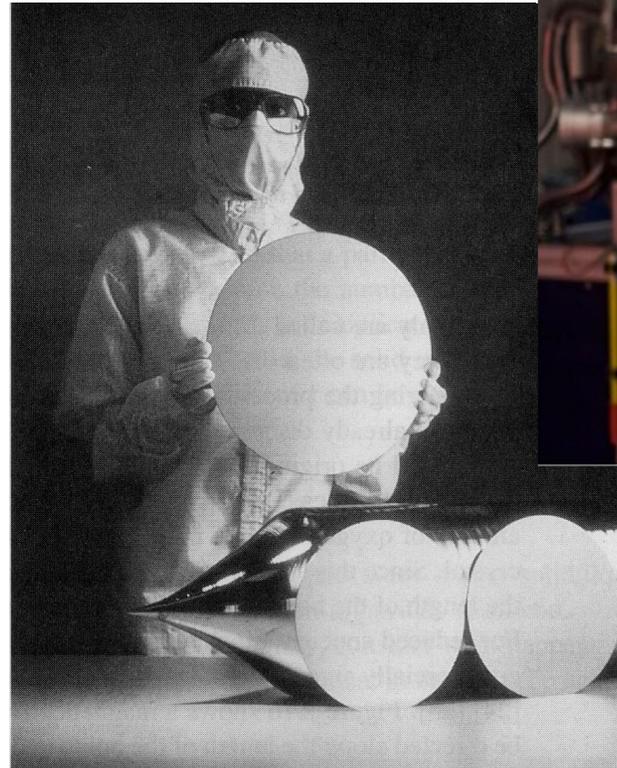
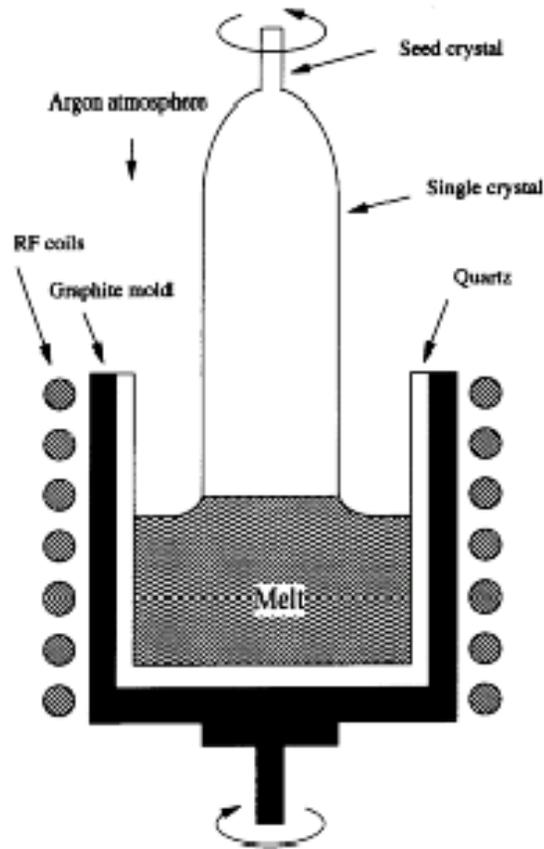
Atoms forming a  
“Semiconductor”

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



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

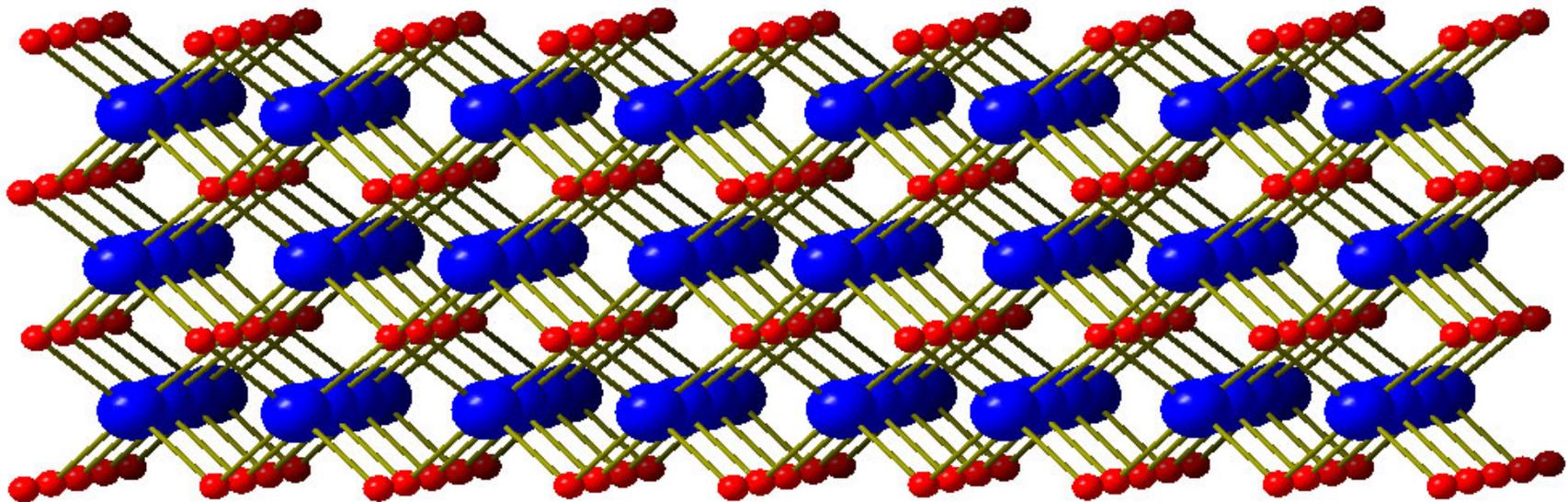
The vast majority of crystalline silicon produced is grown by the Czochralski growth method. In this method, a single crystal seed wafer is brought into contact with a liquid Silicon charge held in a crucible (typically  $\text{SiO}_2$  but may have a lining of silicon-nitride or other material). The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



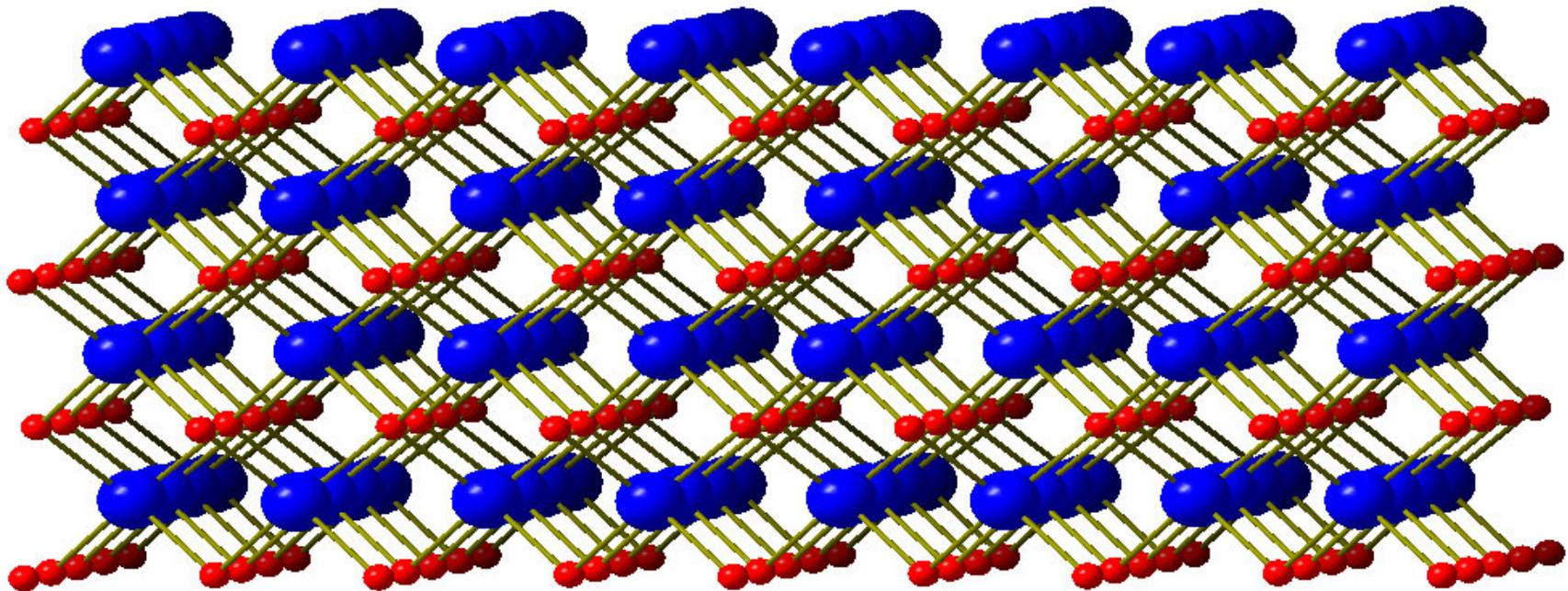
Schematic representation of the Czochralski (a) and float-zone (b) single-crystal growth techniques.

# How do we create Bandgap Engineered Structures? Epitaxy

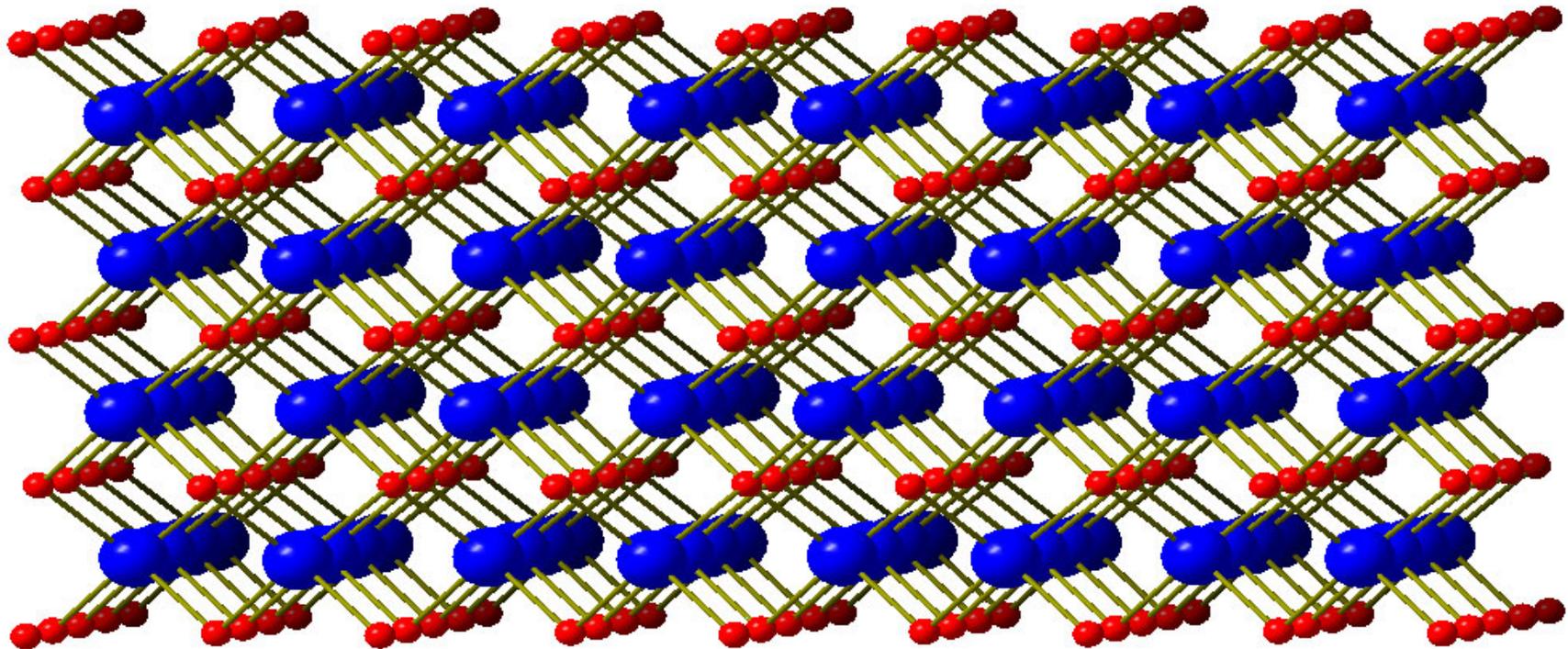
- Repeating a crystalline structure by the atom by atom addition.
- Chemistry controls the epitaxy to insure that, for example, Ga bonds only to N and not Ga-Ga or N-N bonds\*.



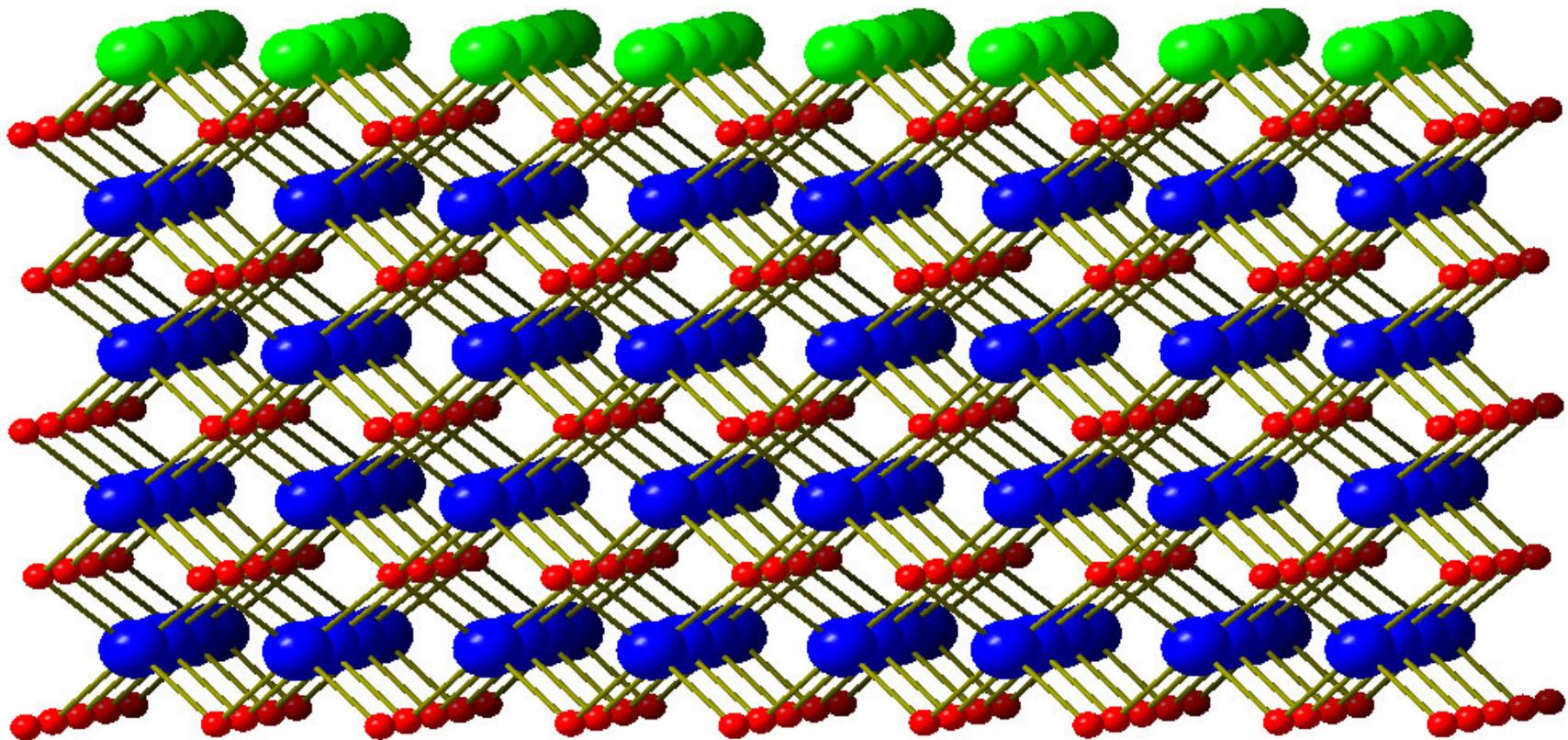
# How do we create Bandgap Engineered Structures? Epitaxy



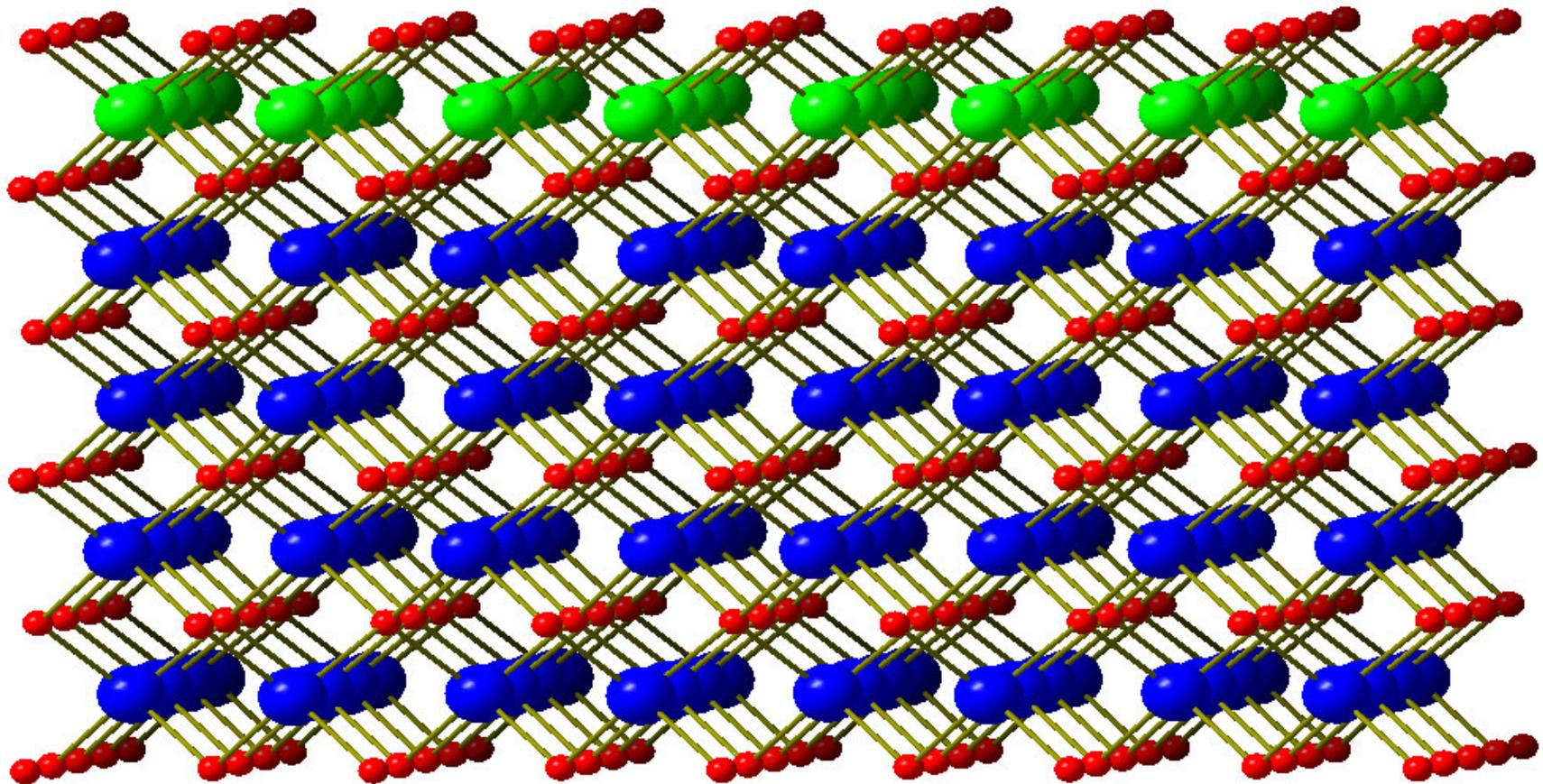
# How do we create Bandgap Engineered Structures? Epitaxy



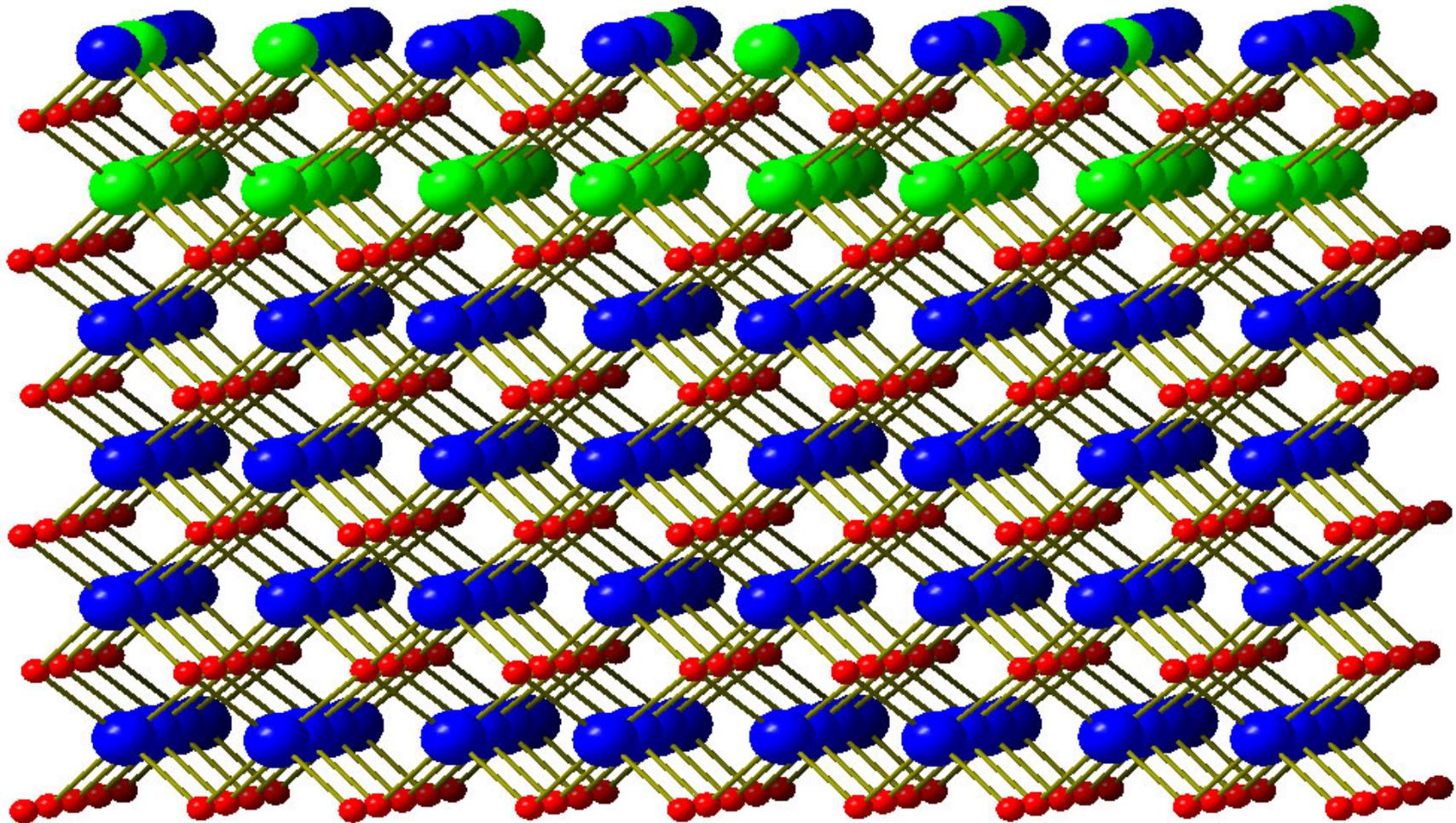
# How do we create Bandgap Engineered Structures? Epitaxy



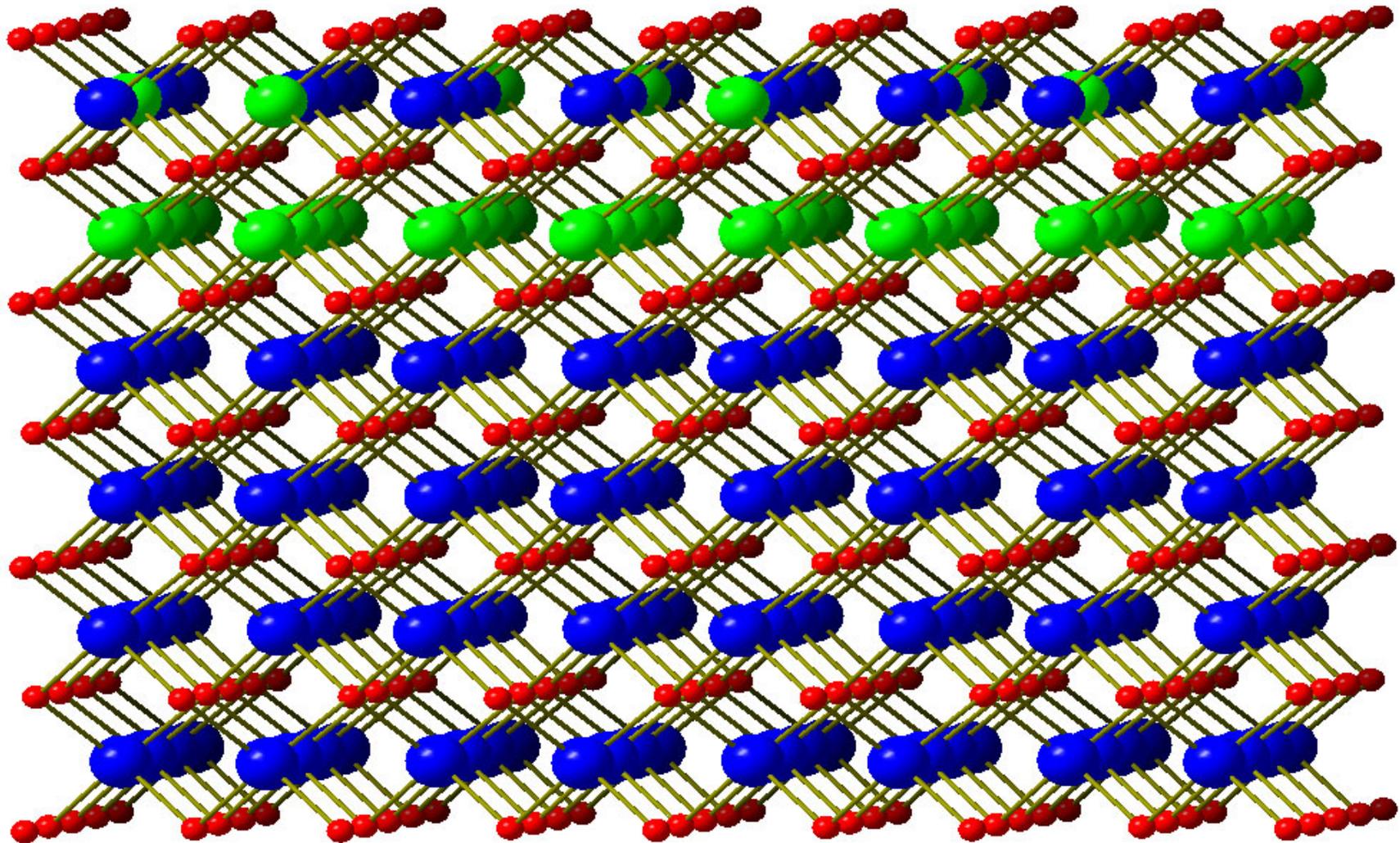
# How do we create Bandgap Engineered Structures? Epitaxy



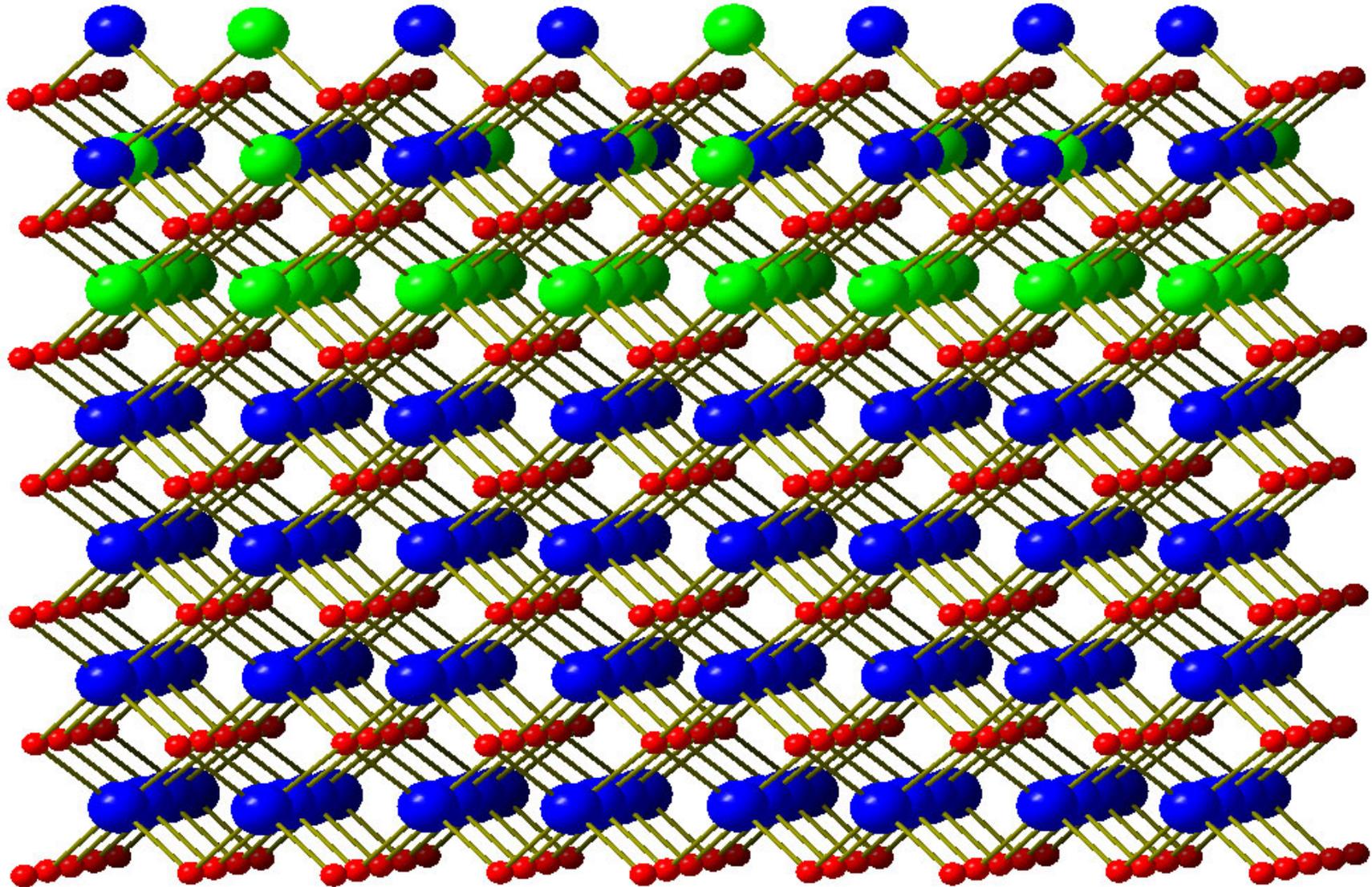
# How do we create Bandgap Engineered Structures? Epitaxy



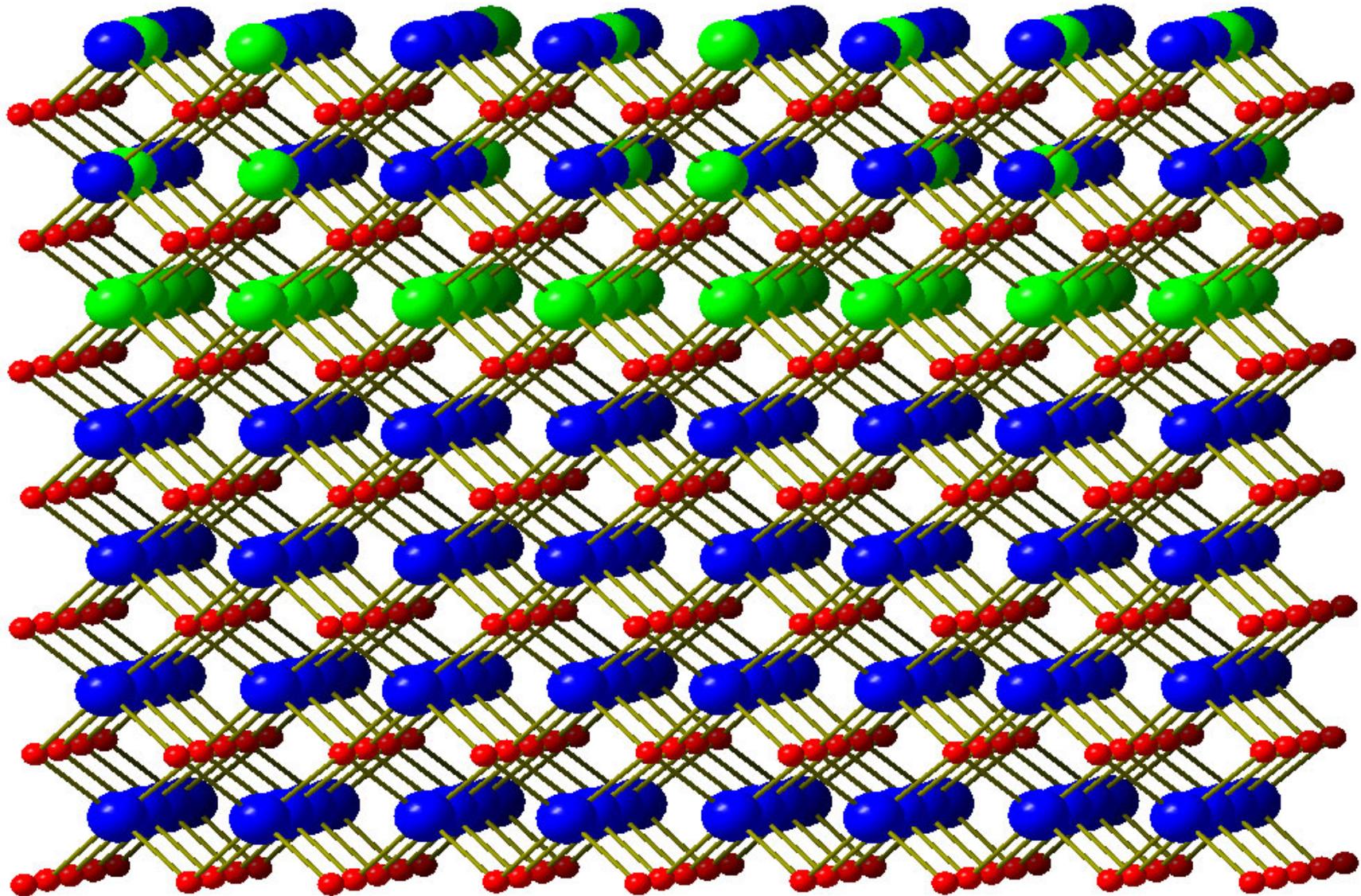
# How do we create Bandgap Engineered Structures? Epitaxy



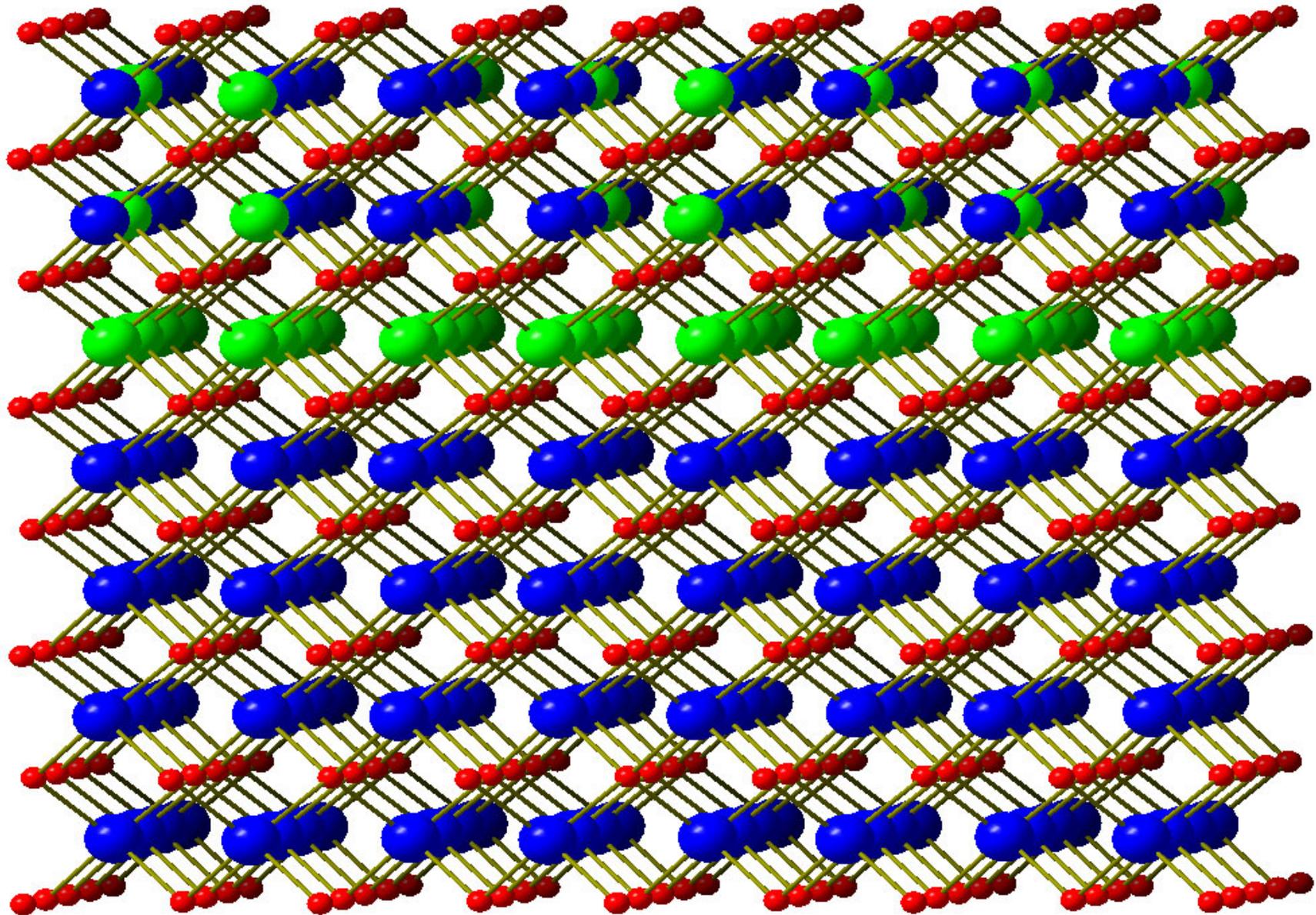
# How do we create Bandgap Engineered Structures? Epitaxy



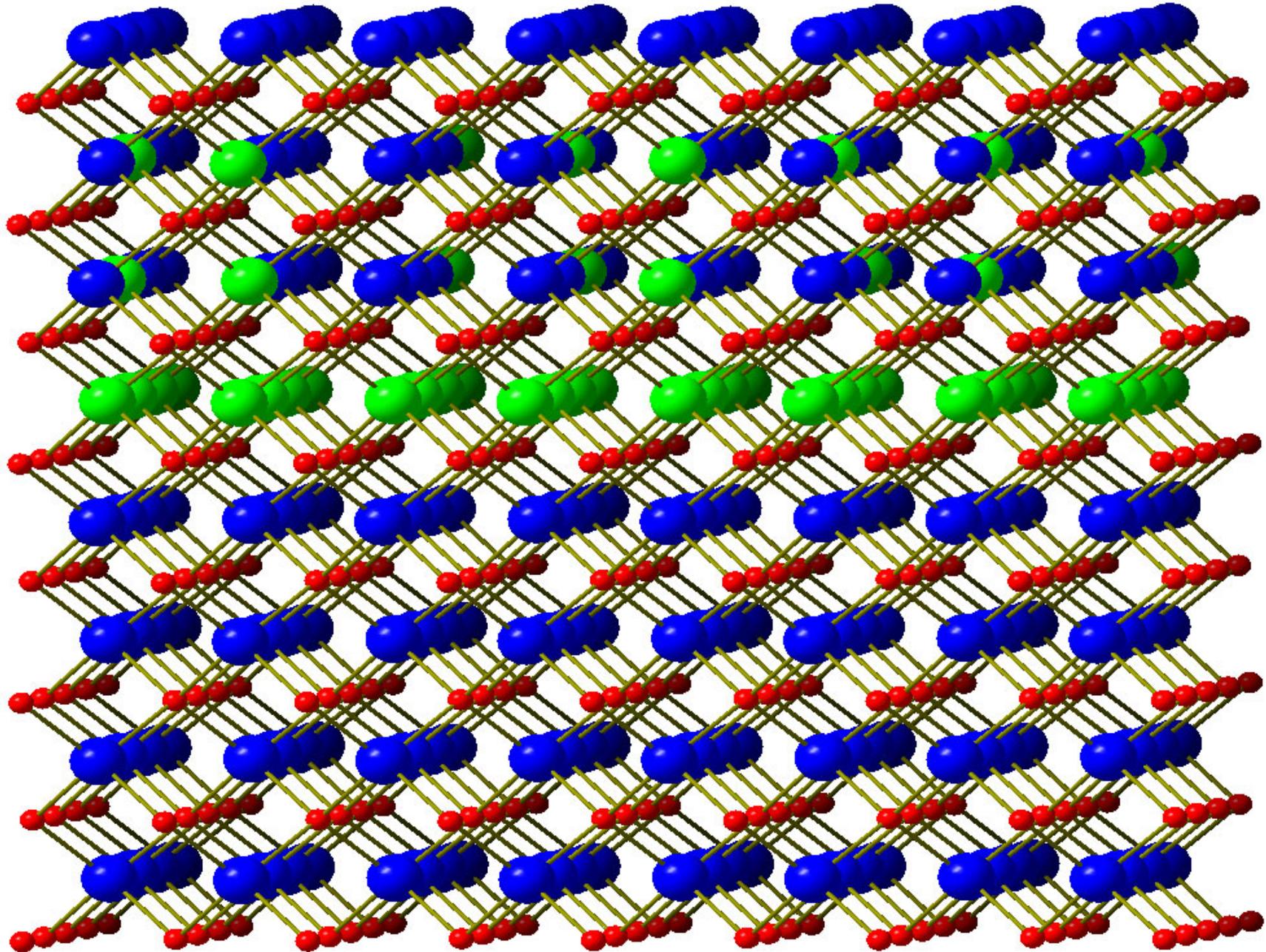
# How do we create Bandgap Engineered Structures? Epitaxy



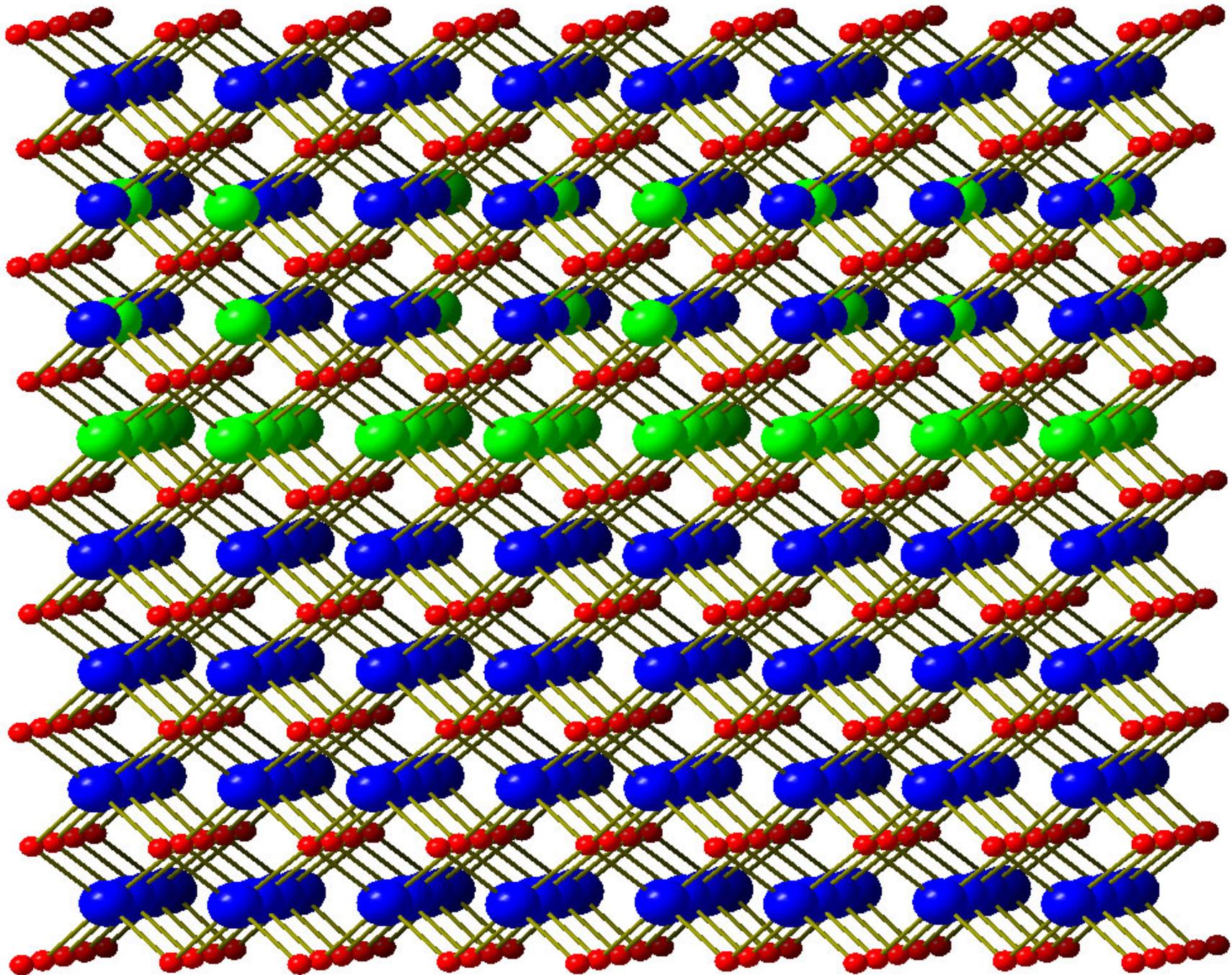
# How do we create Bandgap Engineered Structures? Epitaxy



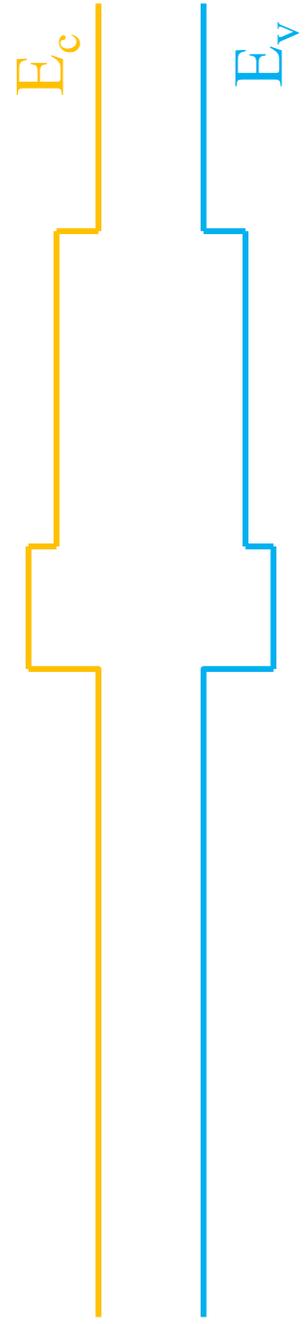
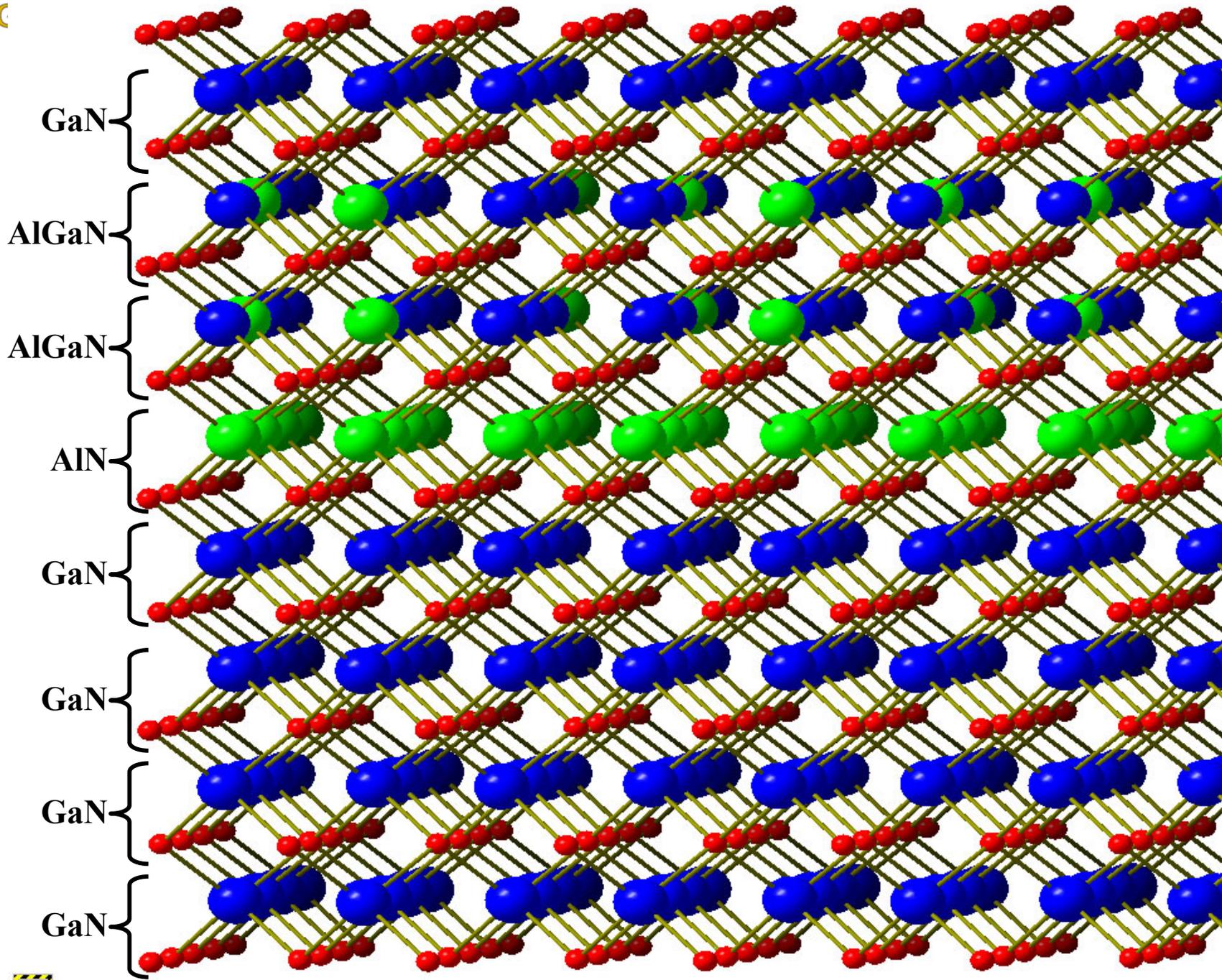
# How do we create Bandgap Engineered Structures? Epitaxy

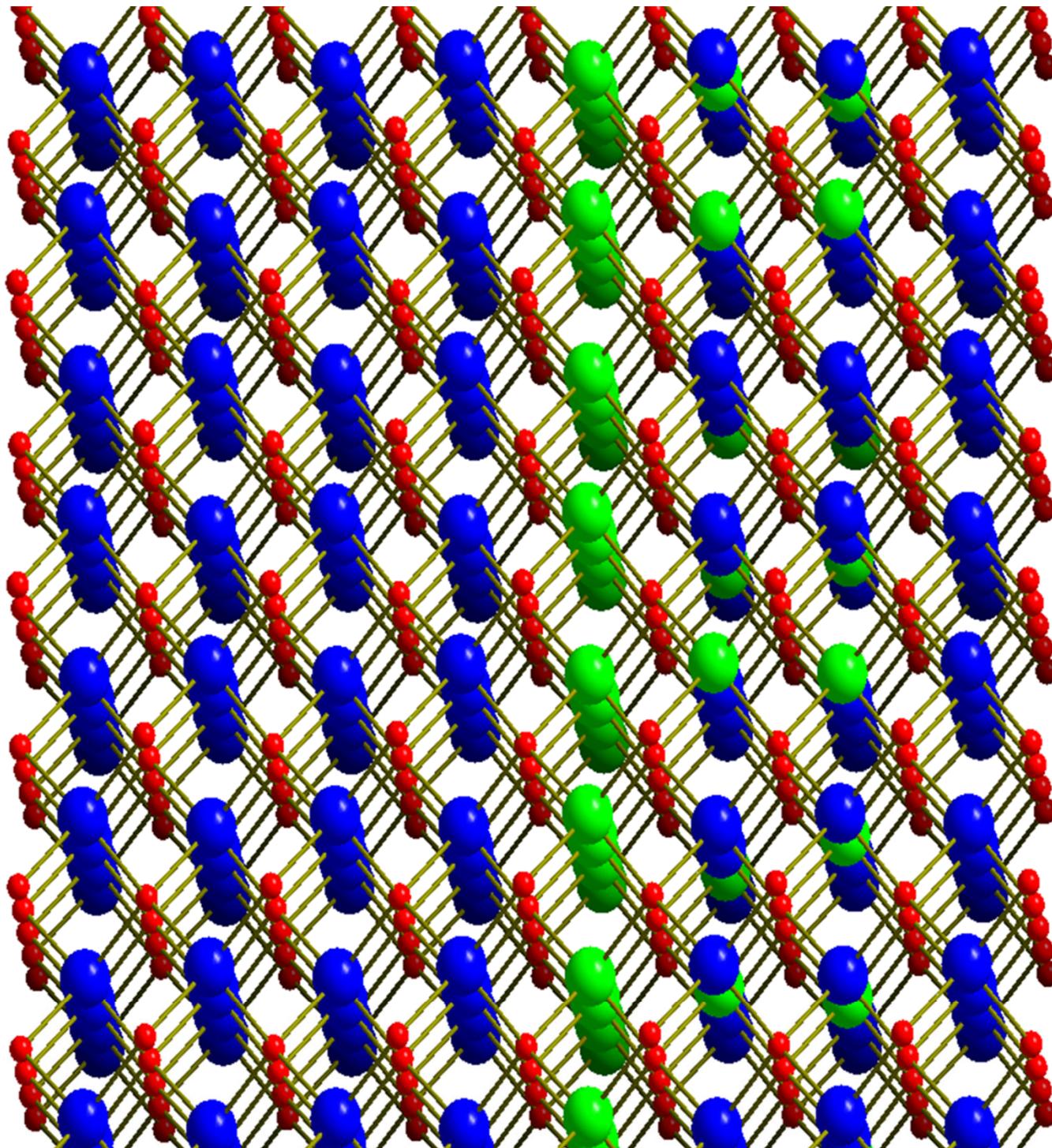


# How do we create Bandgap Engineered Structures? Epitaxy

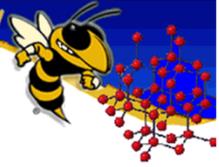


# How do we create Bandgap Engineered Structures? Epitaxy





$E_c$



# MBE

Partially disassembled MBE system for clarity

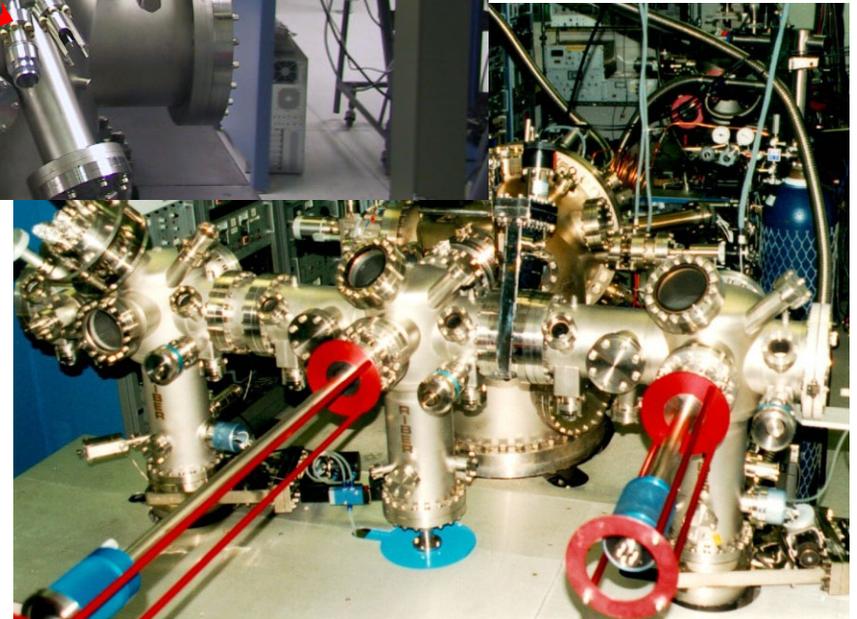
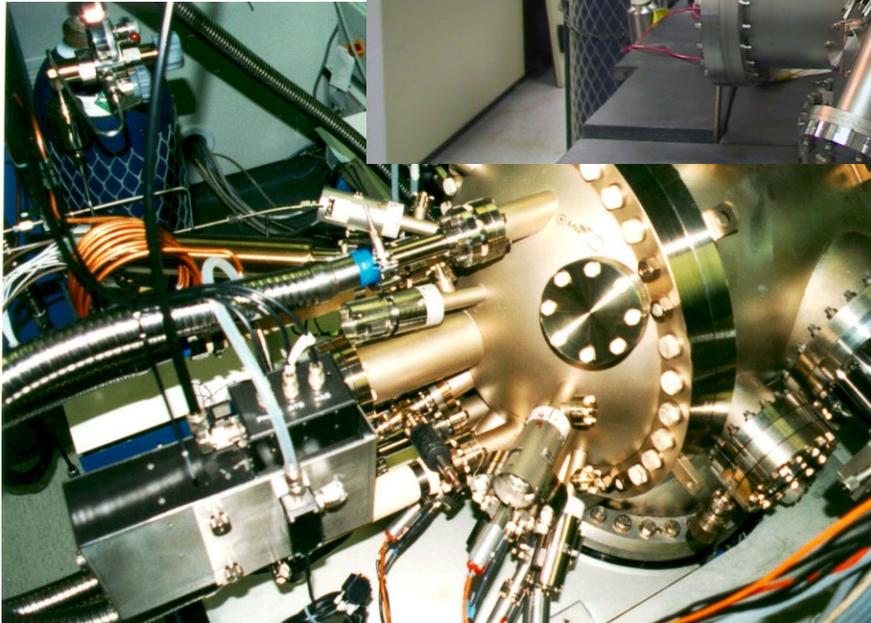


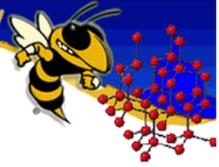
RHEED Gun

Effusion Furnaces

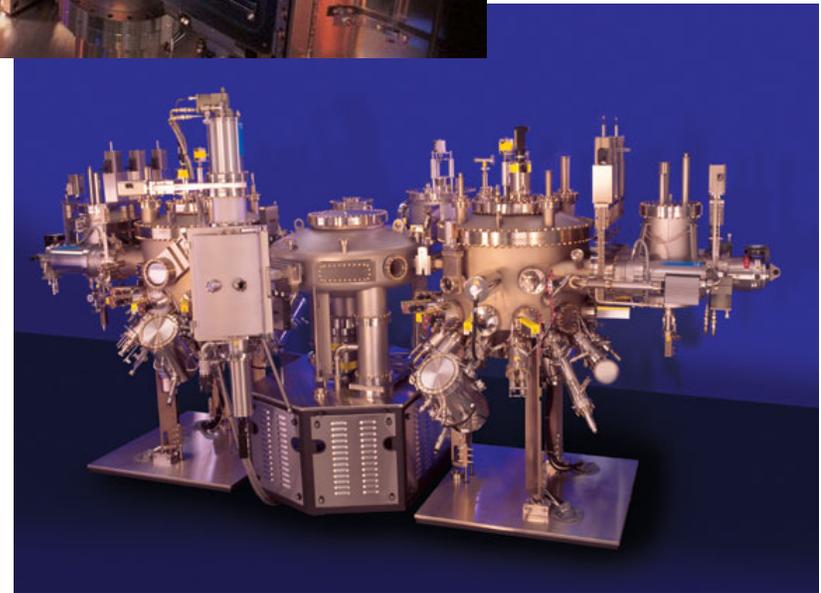
Gas Source (oxygen)

Shutter mechanism





# Commercial Veeco® MBE





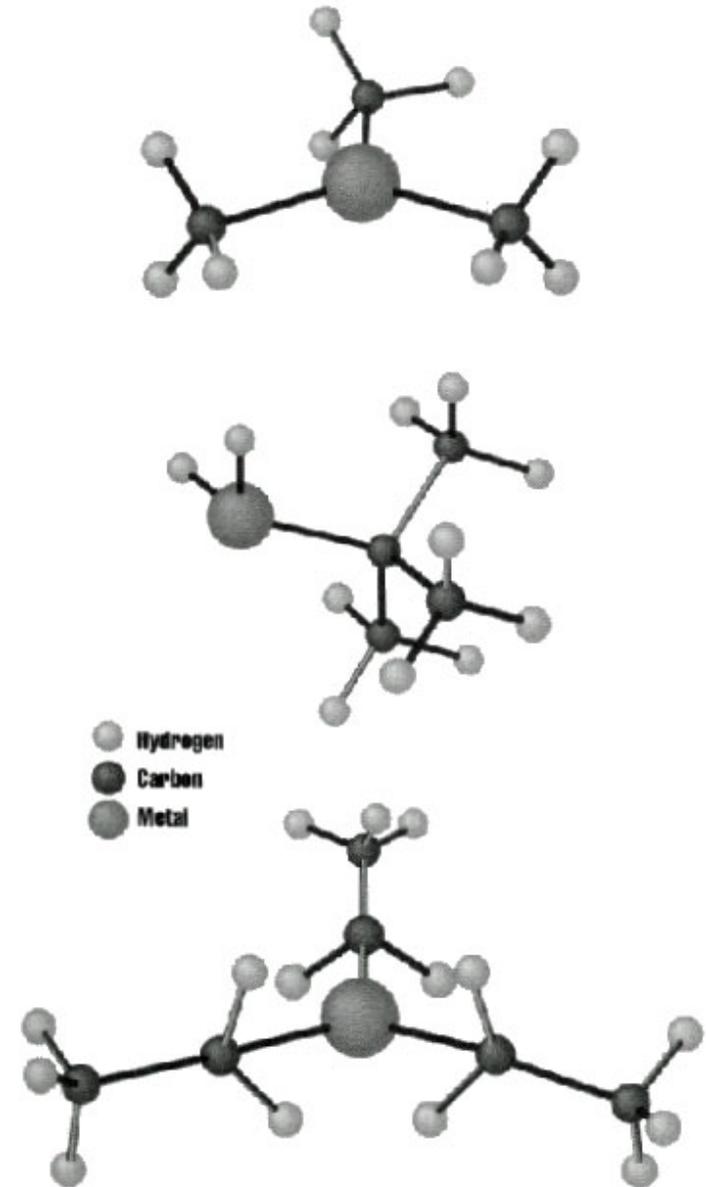
# Alternative Methods: MOCVD

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.

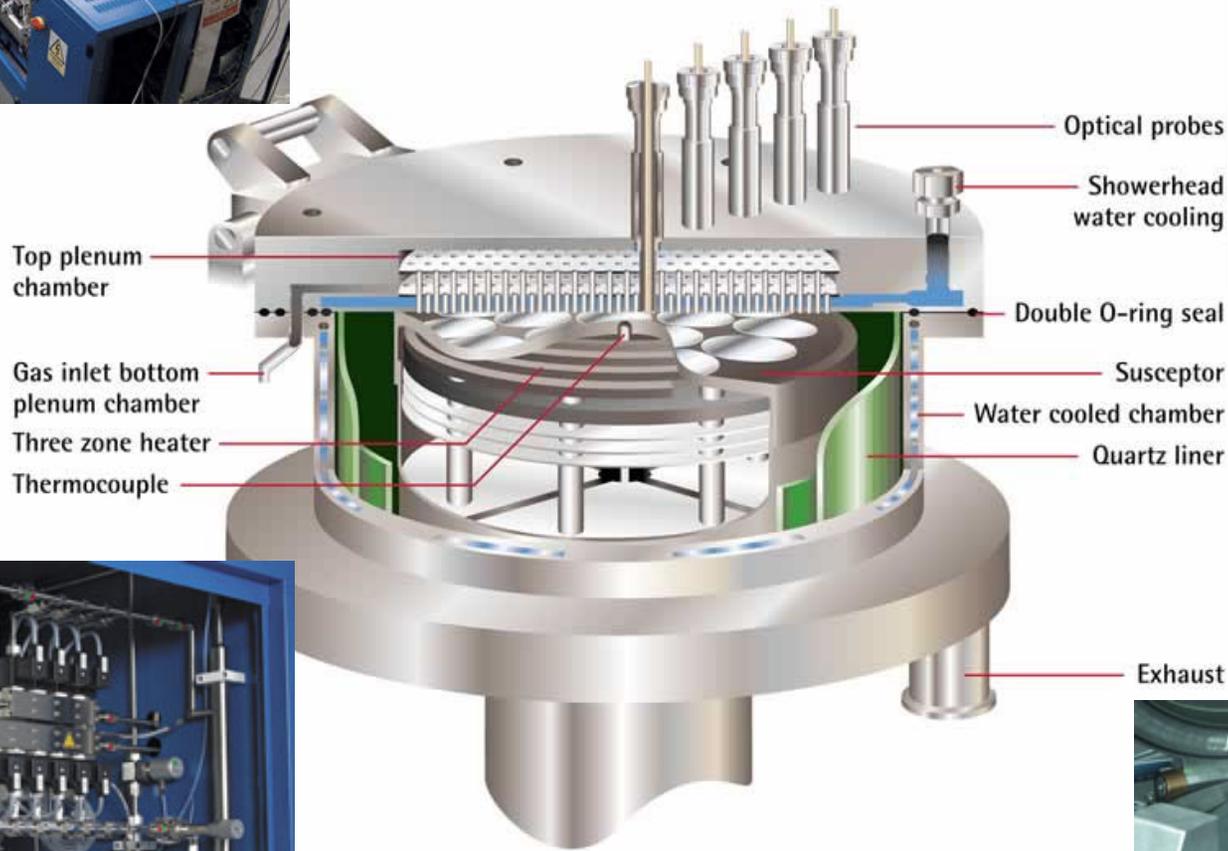
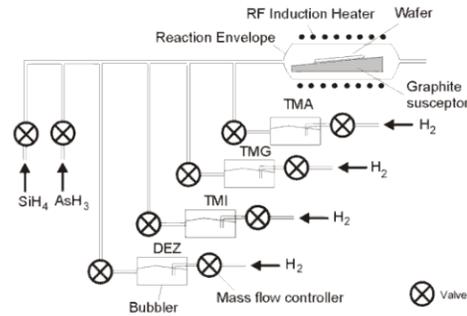
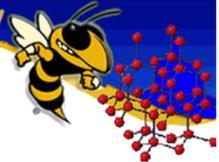
Human Hazard: As the human body absorbs organic compounds very easily, the metal organics are very easily absorbed by humans. Once in the body, the weak metal-organic bond is easily broken, thus, poisoning the body with heavy metals that often can not be easily removed by normal bodily functions. In extreme cases, blood transfusion is the only solution (if caught in time). “Luckily”, such poisoning is rare as the pyrophoric (flammable in air) nature of most metal organic means the “victim” is burned severely before he/she can be contaminated.

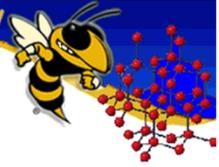


**Figure 14-19** Examples of common organometallics used in MOCVD include (from top to bottom): trimethylgallium, tetrabutylarsine, and triethylgallium.



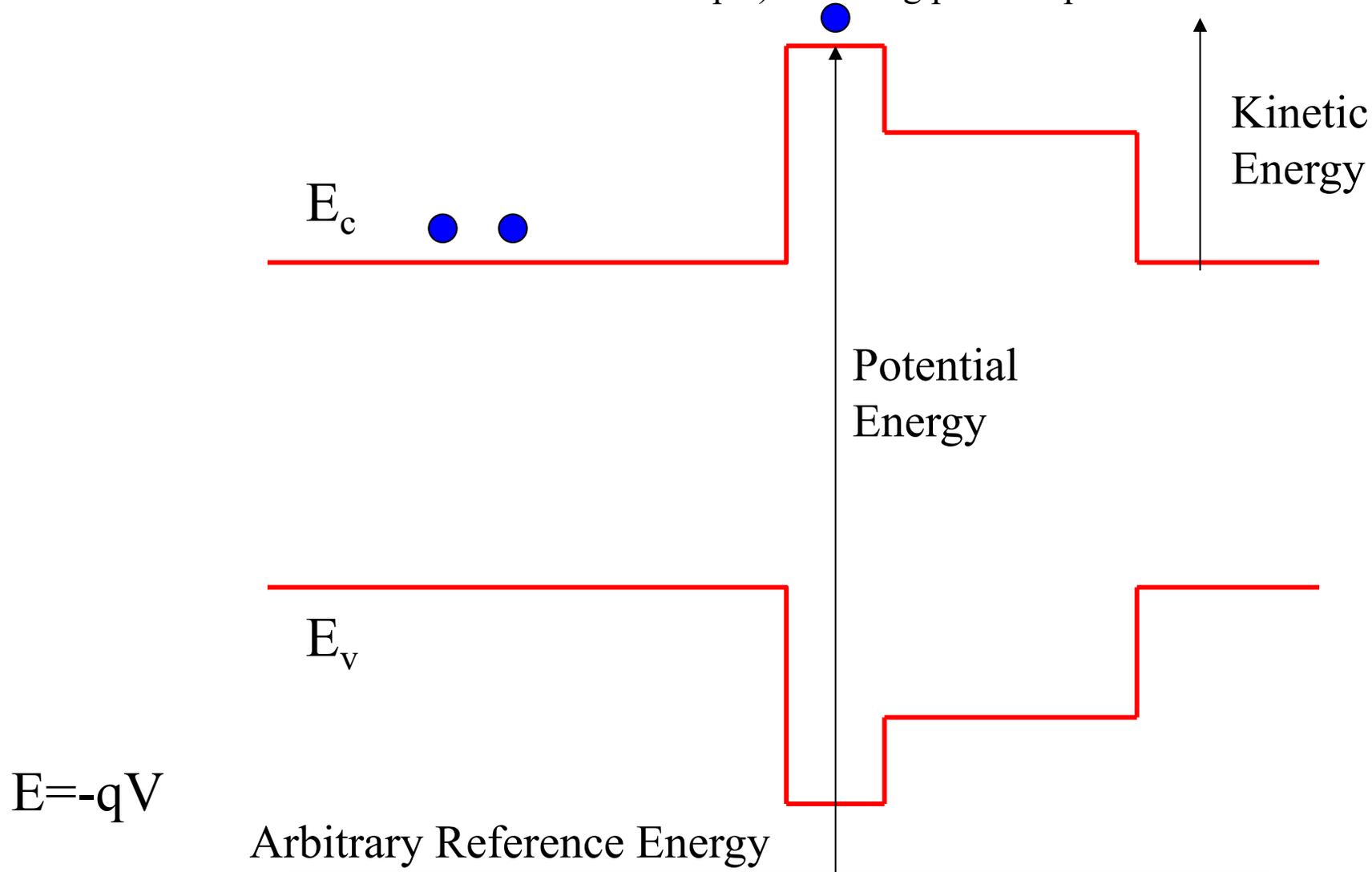
# Commercial Thomas Swan<sup>®</sup> MOCVD

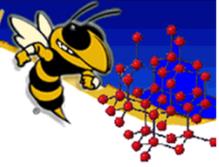




# Engineered Energy Behavior in Compound Semiconductors

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.





**So much for the  
introduction.  
Now on to the  
meat of the  
course.**