

The World of Compound Semiconductors



A Guidebook to the Core Science and Technology

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0.1 Scope

Compound III-V Semiconductors

A new family of semiconductors is changing the way we live. These semiconductors are in our cell phones, in our optical-fiber communications systems, in our CD and DVD players, and soon in our home and office lights. They are called compound semiconductors, because they are compounds of two or more elements.

This book is a guide to the science, technology, and applications of the most important of these semiconductors, composed of one element from column III, and one from column V, of the Periodic Table -- the so-called compound III-V semiconductors, such as GaAs, InP and GaN.

Ia	IIa		IIb	IIIa	IVa	Va	VIIa	VIIIa
H								He
Li	Be			B	C	N	O	Ne
Na	Mg			Al	Si	P	S	Ar
K	Ca		Zn	Ga	Ge	As	Se	Br
Rb	Sr		Cd	In	Sn	Sb	Te	I
Cs	Ba		Hg	Tl	Pb	Bi	Po	At
								Rn

IV's, III-V's, II-VI's, I-VII's

These compound III-V semiconductors are a subset of the universe of simple $A^N B^{8-N}$ binary octet compounds, whose outer orbitals are filled with exactly 8 electrons: the elemental column IV semiconductors Ge, Si and C, the compound II-VI semiconductors such as ZnSe and CdS, and the compound I-VII semiconductor/insulators such as NaCl and LiF.

In many ways, all the semiconductors in the universe of simple octet compounds are similar. As semiconductors, their electrical conductivities are "intermediate" between those of metals and insulators. And, as semiconductors, their electrical conductivities can be modified by electric fields, enabling switching, amplification, and other electronic functions. Hence, if only the simplest semiconducting properties are required, for modest-performance electronics, it is the most abundant, most economical-to-process semiconductor that dominates: the elemental column IV semiconductor Si.

However, in many other ways, the compound III-V semiconductors are unique within the universe of simple octet compounds, enabling them to dominate higher performance electronics and optoelectronics.

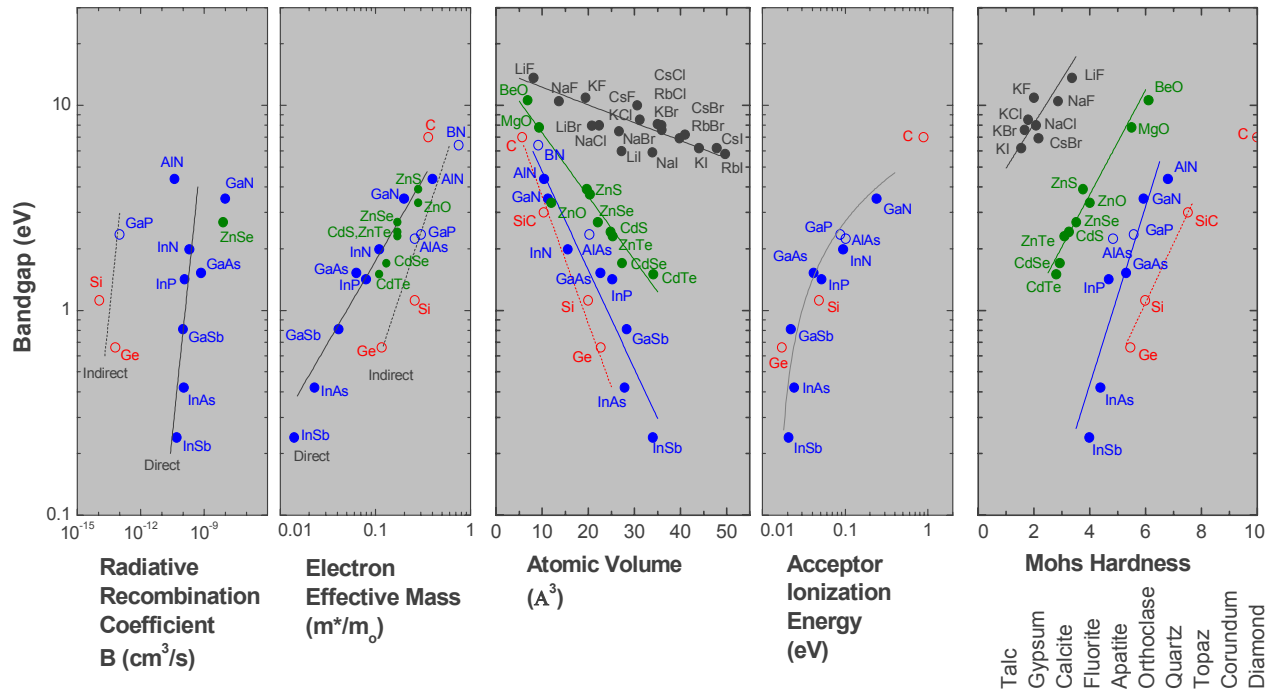
One way to think of this uniqueness is in terms of the trend for bonds between atoms to become more polar in moving "outwards" in the Periodic Table from the column IV semiconductors to the III-V's, II-VI's and I-VII's. These trends are illustrated in the Facing Figure, which shows a visual map of the key properties of the simple binary octet semiconductors.

Direct Bandgaps

There are two *favorable* consequences to the polarity trend. Both stem from the tendency, as bonds become more polar, for bandgaps to become "direct" (filled symbols) rather than "indirect" (open symbols). In other words, electrons at the bottom of the normally-unfilled conduction band have the same $k=0$ momentum as electrons at the top of the normally-filled valence band.

First, valence electrons can absorb photons and become conduction electrons, and conduction electrons can emit photons and become valence electrons, both without phonons that otherwise might be needed to conserve momentum. Moving outwards from Column IV of the Periodic Table, Ge is "indirect," has a lower radiative recombination coefficient, and is less useful for optoelectronics. GaAs and ZnSe are "direct," have higher radiative recombination coefficients, and are more useful for optoelectronics. Hence, today's most efficient and highest-power commercial semiconductor lasers are based on GaAs.

Second, electron masses in the "direct gap" $k=0$ electron states are usually lower than in the "indirect gap" $k \neq 0$ electron states. Ge, which is less ionic, is indirect, and has a higher electron effective mass less useful for high-speed electronics; while GaAs and ZnSe are more ionic, are direct, and have lower electron masses more useful for high-speed electronics. Hence, today's most efficient and highest-speed commercial semiconductor amplifiers are based on GaAs.



Doping and Hardness

There are also two *unfavorable* consequences to the polarity trend.

First, as bonds become more polar, the greater the energy gained upon transferring electrons between atoms, and the wider the bandgap.¹ However, the ionization energies of dopants increase with bandgap, making wider-gap semiconductors much more difficult to dope (especially with acceptors to make p-type material) than narrower-gap semiconductors. Hence, Ge and GaAs, which are less polar, are easy to p-type dope, while ZnSe, which is more polar, is difficult to p-type dope.

Second, as bonds become more polar, their strengths are increasingly determined by electrostatic energies, and depend increasingly less on the angles between bonds. Hence, more-polar semiconductors are less resistant to bond-angle deformation and plastic shear. They are “softer” materials that more easily incorporate defects such as

¹ This is in addition to another trend: for bandgap to increase with decreasing interatomic spacing between the atoms in the lattice. The closer the atoms are to each other (the smaller the volume per atom), the stronger the covalent bonds, and the larger the bandgap.

dislocations. These defects scatter carriers, inhibit photon emission, and enhance device degradation rates. Hence, Ge, which is less polar, has typical substrate dislocation densities of 100 cm⁻², while GaAs and ZnSe, which are more polar, have typical substrate dislocation densities of 1,000 cm⁻² and 10,000 cm⁻², respectively.

Uniqueness of III-V's

The uniqueness and practical importance of the compound III-V semiconductors stems from their balancing of these competing trends. They are polar enough to be direct-bandgap semiconductors, with the accompanying strong interactions with photons useful for optoelectronics and the low electron masses useful for high-speed electronics. But they are not so polar that they cannot be p-type doped or that they suffer from too-high defect densities.

And, within the compound III-V semiconductors, the three that themselves balance these competing trends best are: GaAs, studied extensively since the 1950's; InP, studied extensively since the 1970's; and GaN, studied extensively since the 1990's.

0.2 Audience and Format

Audience

Because of the unique properties of the compound III-V semiconductors, they have been the source of a rich world of science, technology and applications. This world has, on the science side, led to 7 Nobel Prizes in Physics; and, on the applications side, led to a roughly US\$12B global chip market in 2001, projected to become US\$31B in 2006. The NASA “Earth at Night” satellite image shown in the facing figure illustrates a potential new market: the lights, necessary for human civilization, that may someday derive from compound semiconductor chips.

As a consequence, there is a broad and diverse group of people interested in the world of compound III-V semiconductors: perhaps 10,000 technical students and professionals active in the area worldwide, and perhaps an additional 50,000 touched in some significant way by the area. This book is intended to be useful to a large fraction of this audience. To try to accomplish this, there are a number of unique aspects to this book.

1 Core and Inner-Core References

A first unique aspect of this book is that its content is based on a database of highly-cited journal articles and U.S. patents. Hence, the book represents an guidebook to widely accepted “core knowledge,” rather than still-being-debated “frontier knowledge”.² It also represents a guidebook to both science (represented by journal articles) and technology (represented by patents).

The database was created using a combination of key word and key author searches of primary databases,³ followed by citation-number and topic-area culling. In some topic areas, the database was augmented by citation “expansions” (adding articles or patents that cited the initial set followed by additional citation-number and topic-area culling).

² S. Cole, *Making Science: Between Nature and Society* (Harvard University Press, Cambridge, Massachusetts, 1992).

³ For journal articles, we used the Institute of Scientific Information database, and for U.S. patents, we used the Delphion and U.S. Patent Office databases.

Two sets of citation thresholds were used. For inclusion in the core database, the citation thresholds were: 100 for journal articles and 20 for U.S. patents. For inclusion in an “inner-core” database, citation thresholds were: 200 for journal articles and 40 for U.S. patents.

The process used to create the two databases is not foolproof, of course, and certainly some highly-cited references will have been missed. Hopefully, feedback from the technical community will enable improved subsequent editions of this book.

2 Objective Taxonomy

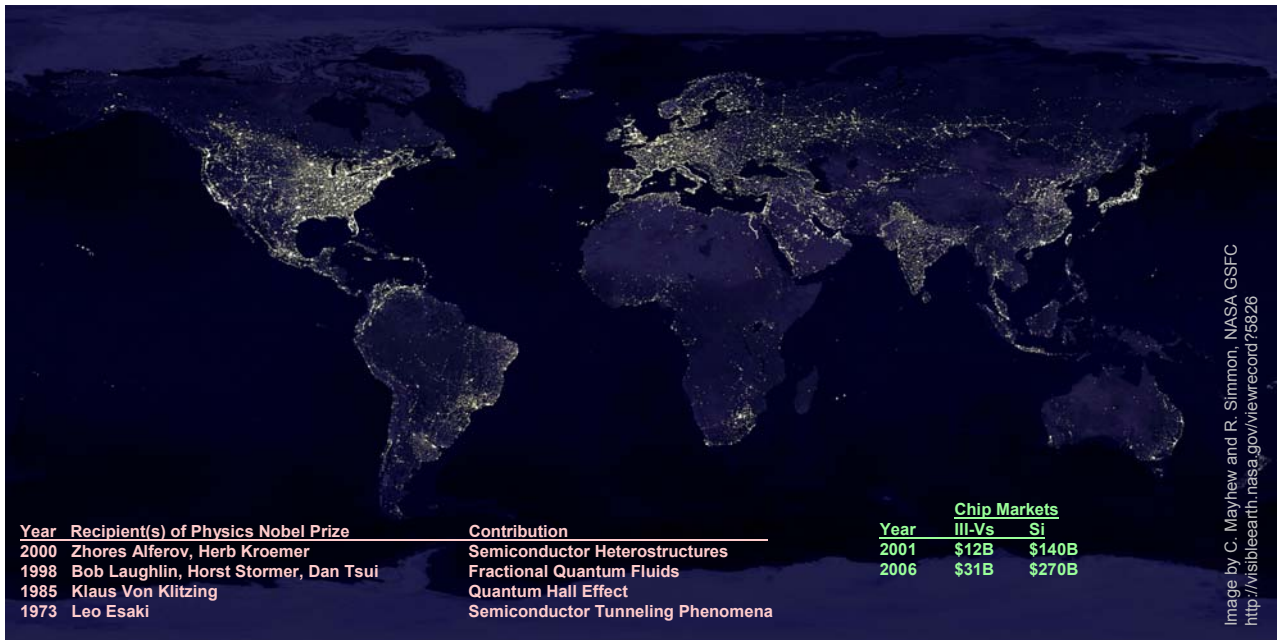
A second unique aspect of this book is that its content is organized around an objective “taxonomy” of the field. Hence, the book represents an unbiased overview, rather than one that emphasizes subfields of special interest to its author.

The taxonomy was created iteratively by (a) mapping the core references into Chapters and Sections and Subsections, and (b) editing the Chapter, Section and Subsection content so that they contained roughly equal numbers⁴ of core references *and* fit together in a technically logical manner.⁵

The resulting Chapter and Section taxonomy is summarized in the Table of Contents. The numbers in parentheses next to the Chapter and Section headings represent the numbers of articles and patents in the core database that map into those particular Chapters or Sections.

⁴ Because the science literature (represented by a major fraction of journal articles) is much larger than the technology literature (represented by both a minor fraction of journal articles and U.S. patents), weighting journal articles the same as U.S. patents during this iterative process would weight the taxonomy heavily towards science. Instead, under the assumption that science and technology are of roughly equal interest to the community, I compensated by weighting U.S. patents somewhat (2.5x) more heavily than journal articles during the iterative process.

⁵ A similar methodology was used to create early drafts of J.Y. Tsao, Ed., *Light Emitting Diodes (LEDs) for General Illumination Update 2002* (Optoelectronics Industry Development Association, Sep 2002).



The taxonomy is doubtless not unique. However, many other taxonomies were tried and found difficult to simultaneously reconcile with the iterative process. Indeed, during the process, the taxonomy evolved in sometimes surprising ways, though the final taxonomy does appear intuitively satisfying.

3 Physical Layout

A third unique aspect of this book is its physical layout. Every Section is composed of exactly 2 facing pages of content, forming a closed, visual unit. This format enables each Section to be self-contained, minimizing the need for page-flipping. It also forces the book to be faithful to the taxonomy, by weighting each Section equally in length.

The content of the 2 pages of each Section is roughly divided into: 1/3 introductory text, 1/3 technical graphic, and 1/3 inner-core references.

The introductory text is written at an intermediate technical level, approximately that of science magazines such as *Scientific American*. Very few equations are used – physics is emphasized over mathematics.

The technical graphic attempts to create a clear visual representation of a key aspect of the content of its Section, in a way that makes physical

relationships clear without mathematics.⁶ Also, by balancing the text with such a technical graphic, the hope is that this book will appeal both to those who assimilate knowledge most naturally through words, as well as to those who assimilate knowledge most naturally through graphics.

The inner-core references are intended to be a high-quality entry point into the original literature defining a particular technical area. They are also intended to appeal to those interested in a snapshot “history” of important scientific and technological contributions. And, they are intended to pay respect to the human creativity and work that underlies those contributions.

Use of Content

The content of this book may be used freely for non-commercial purposes; original source material will be maintained on an accompanying website.

⁶ The graphics have been inspired especially by the work of Prof. Edward Tufte (E.R. Tufte, [The Visual Display of Quantitative Information](#) (Graphics Press, Cheshire, Connecticut, 1983)), who has developed general design principles for technical graphics, and of Prof. Michael Ashby, (M.F. Ashby, [Materials Selection in Mechanical Design](#), 2nd Ed. (Butterworth-Heinemann, Oxford, 1999)), whose materials property “maps” have become elegant tools with which to compare and organize broad families of materials and their physical properties.

0.3 Organization

Overall Organization

The body of this book is divided into twelve chapters: five emphasize physics; three emphasize fabrication; and four emphasize devices and applications.

As illustrated in the facing figure, the relative numbers of core articles and patents mapped onto the various chapters depend substantially on their emphases. The **physics** chapters are weighted towards articles, and can be viewed as having more “science” content. The **device and applications** chapters are weighted towards patents, and can be viewed as having more “technology” content. The **fabrication** chapters are evenly weighted, with some aspects (epitaxy and thin films) having more “science” content, and others (device processing) having more “technology” content.

Within each area (physics, fabrication, devices and applications), the chapters are organized according to the following criteria.

Physics

The physics chapters are organized according to: (a) type of particle (electrons or photons); and (b) dimensionality (3D, 2D, 1D or 0D) of the structure.

At the highest level of classification, electrons, the focus of four chapters, are dominant over photons, the focus of only one chapter. One can think of this as due to the stronger Coulomb and exchange interactions between charged Fermions (such as electrons) compared to the weaker interactions between uncharged Bosons (such as photons or phonons). The strength of these interactions has led to a much richer “physics” associated with electrons than with photons or phonons.

Also at this level of classification, photons, the focus of one chapter, are dominant over phonons, the focus of no chapters. One can think of this as due to photons existing independently of (though interacting with) the semiconductor, so that they can be used as inputs and outputs to and from the semiconductor. This is a necessary condition for use in devices, and has led to a much greater importance associated with photons than with phonons.

At the next level of classification, the physics of electrons in compound semiconductors is roughly equally weighted towards 3D electrons in bulk materials (chapter 1), 2D electrons at heterojunctions (chapter 2), 2D and 1D electrons in nanostructures (chapter 3), and electrons in separate but coupled nanostructures (chapter 4). Note that as the dimensionality of the structure decreases, quantum (or wave) effects become progressively more important, but the chapters are not *organized* around the progressive importance of wave effects.

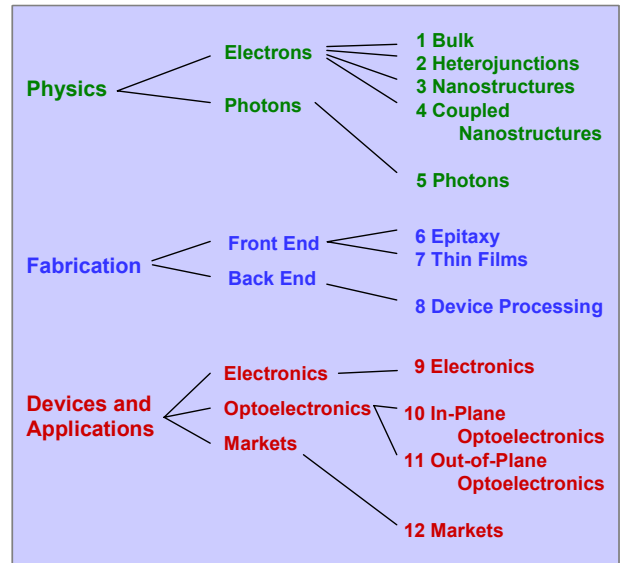
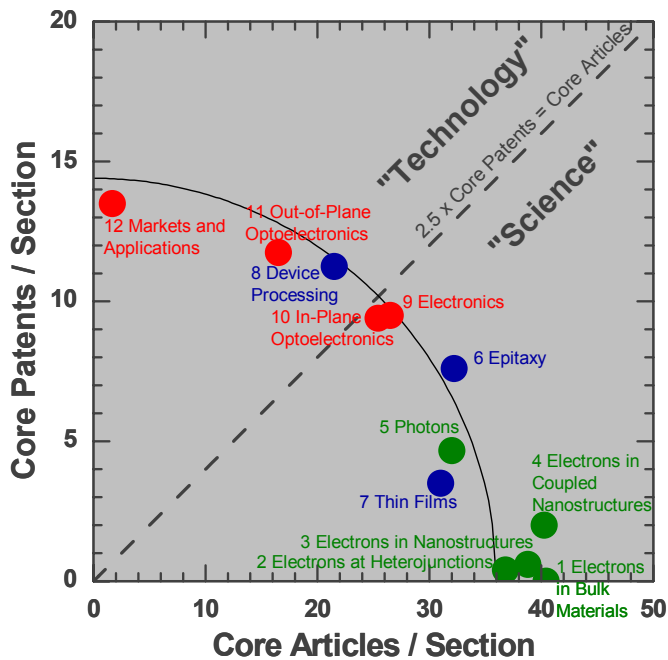
Also at this level of classification, the physics of photons is weighted (in comparison to electrons) more towards 2D and 1D than 3D structures. This can be thought of as due to the much longer wavelengths of photons (0.1-10 μm) than of electrons (0.1-10 nm) -- photons show interesting wave effects in more-easily-fabricated micrometer-scale structures, while electrons only show such effects in less-easily-fabricated nanometer-scale structures.

Fabrication

The fabrication chapters are organized according to: (a) position within the “front-end”-to-“back-end” fabrication flow (from substrates and epitaxy to thin films to thin-film processing); and (b) type of phenomena (surface, thin film or bulk).

At the highest level of classification, “front-end” epitaxy stands out as the single most important fabrication process, even though it is in principle only one of many processes necessary to fabricate a finished device. One can think of this as due to the technical challenges and richness associated with depositing atoms epitaxially (rather than non-epitaxially) as near-perfect thin films on single-crystal surfaces, combined with the importance of these near-perfect thin films to vertically-layered structures that exhibit 2D or 1D physical phenomena.

Hence, two chapters are devoted to epitaxy. One is devoted to those aspects of epitaxy that involve tools (molecular beam epitaxy and organometallic vapor phase epitaxy) and how those tools interact with surfaces. The other is devoted to those aspects of epitaxy that involve materials issues associated with the resulting vertically layered thin films.



Also at this level of classification, “back-end” thin-film processing is of less importance, though it is the focus of one chapter. One can think of this as due to the similarity of processing epitaxial compound semiconductor wafers into laterally patterned devices to that of processing non-epitaxial silicon wafers into laterally patterned devices. The literature associated with silicon device processing is huge, but that unique to compound III-V semiconductors device processing is more modest.

Devices and Applications

The device and applications chapters are organized according to: (a) type of particle (electrons, photons or both); (b) direction of electron or photon motion (perpendicular or parallel to the surface); and (c) end-use application.

At this level of classification, devices that involve both electrons and photons dominate those that involve only electrons. Hence, only one chapter is devoted to electronic devices, while two chapters are devoted to optoelectronic devices. One can think of this as due to the similarity of compound semiconductor electronic devices to their silicon counterparts, and a lack of unique features associated with compound semiconductor electronics. One can also think of this as due to the inability of indirect-gap silicon materials to produce light efficiently, hence the special importance of compound semiconductors in optoelectronics.

An interesting observation, then, is that the unique physics associated with compound III-V semiconductors is dominated by electrons, but the unique devices associated with compound III-V semiconductors are dominated by photons.

At the next level of classification, there is a relatively even weighting between devices in which the direction of electron or photon flow is in-plane or out-of-plane. This is unlike silicon, where the overwhelmingly most important device, the MOSFET (metal-oxide-semiconductor field-effect transistor) is one in which the dominant electron flow is in-plane. One can think of this as due, in the compound semiconductors, to a richer materials base for epitaxial heterostructure engineering, which is especially well-suited to tailoring of out-of-plane transport.⁷

⁷ H. Kroemer, "Heterostructure Bipolar-Transistors and Integrated-Circuits," Proceedings of the IEEE **70**, 13-25 (1982).

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1 ELECTRONS IN BULK MATERIALS (202,0)

Electrons, Ions and Photons in Electric and Magnetic Fields

Electrons are arguably the most important of the three particles – electrons, photons, ions – involved in compound semiconductor physics. Unlike photons, electrons are charged, hence interact strongly with each other and with electric fields, and can be easily controlled and measured externally. Unlike ions, they have very low mass, and can move macroscopic (mm) distances in the microscopic (ns) times of interest for device applications.

Also, though electrons have both charge and spin, their interactions with electric fields are many orders of magnitude larger than their interactions with magnetic fields. Hence, although there has been some recent interest in magnetic semiconductors, the physics of electrons is dominated by the physics of electrons interacting with electric fields.

In this Chapter, we discuss the physics of electrons in bulk materials, interacting with and through, electric fields. This physics, in turn, can be simplified by three major approximations, around which the sections of this Chapter are organized.

Ion Cores and Valence Electrons

The first approximation is that there are two kinds of electrons in the atoms that make up the semiconductor lattice.

The electrons in completely filled inner shells, combined with the atom nucleus they are tightly bound to, form the inert “ion cores.” These ion cores interact relatively weakly with the other ion cores of the lattice.

The electrons in the partially filled outer shell are relatively weakly bound to the atom’s nucleus, and

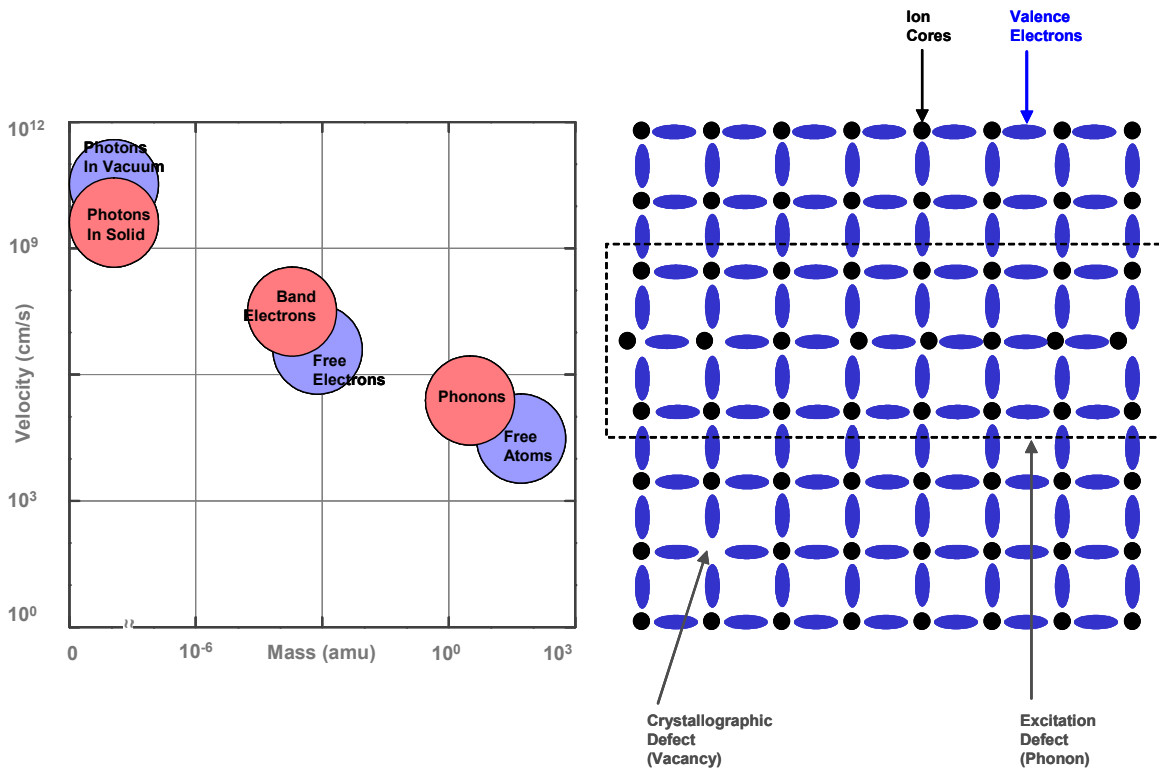
form the reactive “valence electrons.” These valence electrons interact relatively strongly with the valence electrons of the other atoms of the lattice. Through these interactions, the valence electrons are responsible for the bonding between the atoms in the lattice. This bonding, discussed in Section 1.1, determines most of the important lattice properties of the semiconductor, such as its energy of formation, its lattice constant at equilibrium and under stress, its vibrational spectrum, and its polarity.

Born-Oppenheimer Approximation

The second approximation is that the two constituents of the semiconductor – the ion cores that form the lattice, and the valence electrons that form the bonds between the ion cores of the lattice – have very different masses and very different response times to perturbations. The ion cores are roughly 1000x² heavier than the valence electrons, and move 1000x more slowly. As a consequence, the lattice can be considered static on the time scale of electron motion and for the purpose of calculating electron energies.

In this Born-Oppenheimer approximation, the valence electrons can be viewed as interacting with themselves against a backdrop of static ion cores. Through these interactions, the electron band structure is derived – the valence band, derived from valence electrons interacting to form bonding orbitals, and the conduction band, derived from valence electrons interacting to form anti-bonding orbitals. This electron band structure and its dependence on composition and strain, are discussed in Section 1.2.

Periodicity and Deviations from Periodicity



The third approximation is that the ion cores that form the lattice are periodic. Hence, once the electron band structure has been calculated assuming a periodic lattice, electrons occupying these bands interact with the lattice only through deviations from that periodicity. The interactions of electrons with crystallographic deviations from periodicity, such as point defects and defect centers, are discussed in Sections 1.3 and 1.4. The interactions of electrons with “transient” deviations from periodicity, such as other electrons, lattice vibrations (phonons), and photons, are discussed in section 1.5.

1.1 Electrons in Bonds (27)

Bonds and Energies (9)

All compound semiconductor phenomena take place against a backdrop of atoms, and of the bonds between them. These bonds can be understood, to a good approximation, as electrons occupying linear combinations of atomic orbitals. For the simple ANB^{3-N} octet compounds, the relevant orbitals are the one inner-shell s and three outer-shell p orbitals, from which are derived four tetrahedrally oriented sp^3 hybrid h orbitals.

The h orbitals associated with the cation (column III) and anion (column V) atoms of the compound define three energies: (a) an average energy difference, V_1 , between the p and s orbitals; (b) an energy difference, $2V_3$, between the hybrid sp^3 orbitals; and (c) an energy splitting, $2(V_2^2+V_3^2)^{1/2}$, between the bonding and antibonding orbitals that form as the cation and anion approach each other.

The relative magnitudes of these three energies define three physical scales: (1) bond polarity ($V_3/[V_2^2+V_3^2]^{1/2}$) -- the tendency of electrons to be transferred from cation to anion, and for bonding to be partly electrostatic; (2) bond covalency ($V_2/[V_2^2+V_3^2]^{1/2}$) -- the complement to bond polarity; and (3) bond metallicity ($1.11V_1/[V_2^2+V_3^2]^{1/2}$) -- the tendency of the gap between the bonding (valence) and anti-bonding (conduction) bands, and the energy necessary for an electron to freely wander through the solid, to disappear.

Many of the lattice properties of the compound semiconductors can be understood through the energies V_1 , V_2 and V_3 , and their related physical scales of bond polarity, covalency and metallicity.

Elasticity (8)

A first example is mechanical properties -- the resistance of lattices to deformation. Covalent bonding is directional (depends on bond angle), while polar bonding is not. Hence, as polarity increases, the ratio between the force constants that resist bond bending (β) and stretching (α) decreases. Likewise, those mechanical properties (e.g., shear modulus and strength) that involve bond bending weaken, while those (e.g., bulk modulus) that involve mostly bond stretching do not.

Piezoelasticity (4)

A second example is piezoelectricity -- the creation of electric fields by elastic deformation. The cations and anions in a compound semiconductor sit on separate, interpenetrating sublattices. These sublattices can move with respect to each other, and if the cations and anions are charged, piezoelectric fields will develop.

The transverse effective charge, e^*_T , that connects these piezoelectric fields with the sublattice motions depends both on ΔZ , the difference between the cation and anion column numbers in the periodic table, and on polarity. For a completely covalent III-V semiconductor, the effective anion charge would be $+1e$; for a completely polar III-V semiconductor, the effective anion charge would be $-3e$. Hence, as polarity increases, the transverse effective charge increases, and along with it all effects related to piezoelectric fields, including electron-phonon and photon-phonon interactions.

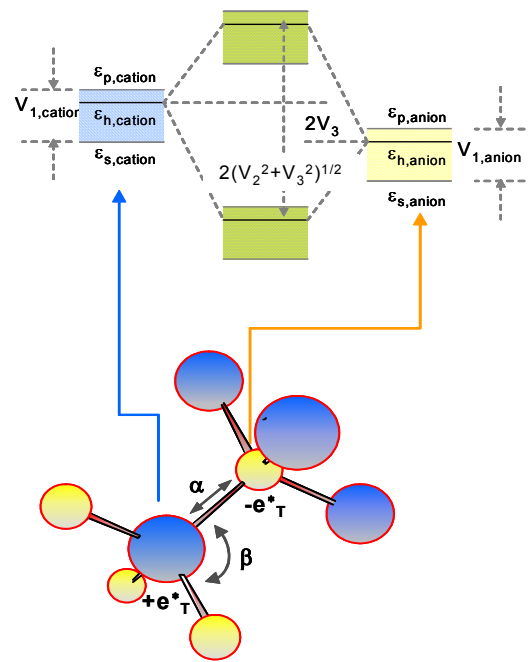
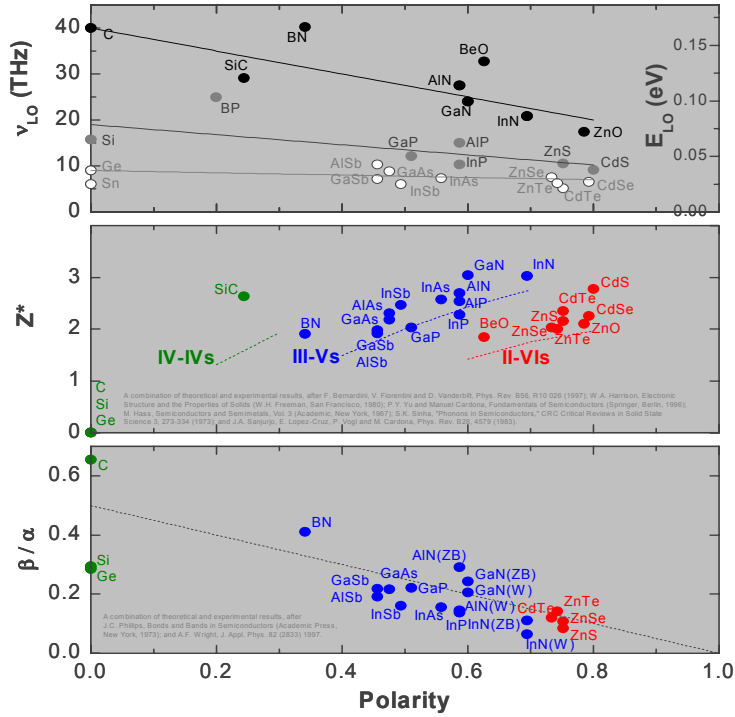
Phonons (6)

A third example is phonons -- the vibrations of lattices. As with any springlike vibration, the lighter the atoms and the stronger the bonds between atoms (the larger V_2), the higher the frequencies of these vibrations. Hence, lattices composed of atoms from higher rows in the periodic table have higher vibrational frequencies than those from lower rows.

This is true for both acoustic (where cations and anions vibrate in phase) and optical (where cations and anions vibrate out of phase) phonons. Hence, sound velocities and thermal conductivities, which increase with increasing acoustic phonon frequency, are higher in lattices composed of atoms from higher rows. Likewise, saturation electron velocities, often limited by longitudinal optical phonon emission, are higher in lattices composed of atoms from higher rows.

Inner-Core Articles

232. F. Bernardini, V. Fiorentini, and D. Vanderbilt, "Spontaneous Polarization and Piezoelectric Constants of III-V Nitrides," *Physical Review B-Condensed Matter* Vol. 56 No. 16 (October 15, 1997) 10024-27.



222. O.H. Nielsen and R.M. Martin, "Stresses in Semiconductors: Ab Initio Calculations on Si, Ge, and GaAs," Physical Review B-Condensed Matter Vol. 32 No. 6 (September 15, 1985) 3792-805 .

209. W.A. Harrison, "New Tight-Binding Parameters for Covalent Solids Obtained Louie Peripheral States," Physical Review B-Condensed Matter Vol. 24 No. 10 (November 15, 1981) 5835-43.

1.2 Electrons in the Lattice (48)

Electron Band Calculations (12)

As discussed in Section 2.1, the valence electrons of the lattice reside in the bonding and anti-bonding orbitals between the atoms of the lattice. Because electrons in neighboring bonds interact strongly, it is convenient to describe them as waves distributed through the lattice. How the energies of these waves depend on k -vector (crystal momentum) is the electron band structure.

This band structure is usually calculated using one of three methods: (1) the LCAO (linear combination of atomic orbitals) or tight binding method, which begins with atomic orbitals and combines them into itinerant wavefunctions; (2) the NFE (nearly-free electron) pseudopotential method, which begins with free electrons and perturbs them with pseudopotentials at the ion cores; and (3) the “ k dot p ” method, which begins with high-symmetry points in k -space, and uses perturbation theory to calculate curvature around those points.

Electron Band Structure (10)

In the facing Figure, the electron band structure of GaAs is shown projected onto line segments connecting various high-symmetry points at the boundaries of the (first) Brillouin Zone in k -space.

The most important bands are the top-most occupied valence band (in green), dominated by bonding orbitals, and the bottom-most unoccupied conduction band (in purple), dominated by anti-bonding orbitals. Because both bands are derived primarily from s -like (lower energy) and p -like (higher energy) atomic orbitals, the bottom of the conduction band is s -like and non-degenerate, while the top of the valence band is p -like and three-fold degenerate (unless split by spin-orbit or other non-centrosymmetric perturbations).

Electron Bandgaps (23)

The most important feature of the electron band structure is the electron band gap -- the energy required to excite an electron from the top of the valence band to the bottom of the conduction band. There are both momentum and energy changes associated with this bandgap.

Momentum Changes. If, as is the case for GaAs, the lowest-energy electron states in the conduction

band have the same $k=0$ momentum as the highest-energy electron states in the valence band, then no momentum change is associated with the bandgap. The bandgap is “direct,” and electron transitions across it are relatively fast.

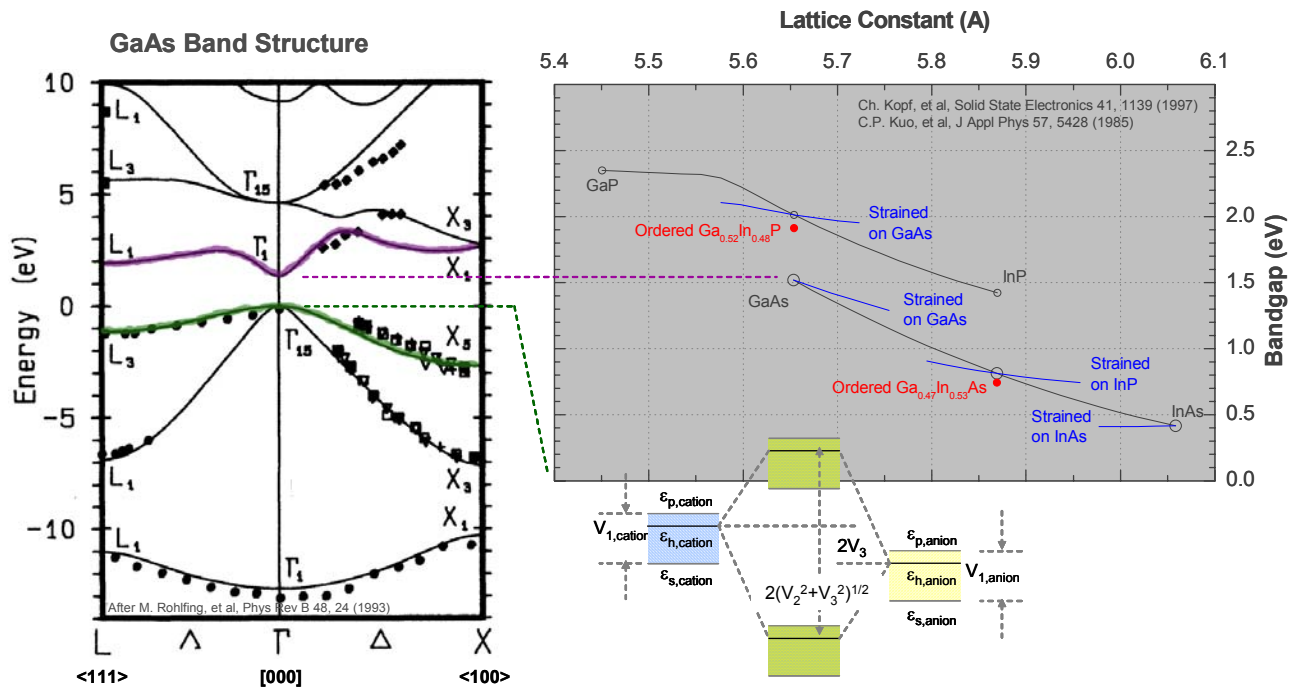
If they do not have the same momentum, then there *is* a momentum change associated with the bandgap. The bandgap is “indirect,” and electron transitions across the bandgap are relatively slow, requiring momentum-conserving additional particles, such as phonons.

Energy Changes. The energy change associated with the bandgap increases with (a) the strength of the covalent bond, V_2 , which in turn increases with decreasing bond length, and (b) the anion-cation electronegativity difference, V_3 . Hence, binary compound semiconductors formed from elements having lower atomic numbers (shorter bond lengths) and larger electronegativity differences have wider bandgaps. And, perturbations which decrease bond lengths (higher hydrostatic pressure or lower temperature) increase bandgaps.

The electron bandgaps of layers used in device heterostructures can be tuned in various ways.

One way is through mixing binary compounds into ternary or quaternary alloys. The resulting bandgaps can be thought of as linear interpolations between those of the endpoint binaries, plus a quadratic deviation (or bowing) towards lower energies. The degree of bowing increases with the difference between the equilibrium lattice parameters of the endpoint binaries, in large part due to relaxation of microscopic internal strain. The degree of bowing also increases in ternary or quaternary alloys that are ordered, in large part due to an *enhanced* relaxation of microscopic internal strain.

Another way is through integration onto substrates having a different equilibrium lattice constant. The resulting in-plane (and associated oppositely-signed out-of-plane) strain decreases bandgaps for compressive bond-shortening strain and increases bandgaps for tensile bond-lengthening strain.



Effective Masses (3)

The next most important feature of the electron band structure is the curvature of the bands at zone center, inversely proportional to the electron and hole effective masses: $d^2E/dk^2 = \hbar^2/m^*$. In k dot p theory, the lower the bandgap, the greater the repulsion between the conduction and valence bands, and the higher the curvature away from zone center. Hence, as illustrated in Section 2.3, effective masses increase with bandgap.

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1.3 Electrons and Point Defects (67)

Point Defects (7)

As discussed in Section 8.2, all semiconductor lattices have point defects. Some are “intrinsic” defects native to the pure semiconductor (e.g., vacancies, interstitials, antisites). Some are “extrinsic” defects due to foreign impurity atoms accidentally or intentionally placed in the lattice (e.g., substitutionals, interstitials).

Point defects can exist in multiple charge states, depending on the Fermi level (or “electrochemical potential”) for electrons in the lattice. When the Fermi level is low, the defect donates electrons to the lattice; when high, it accepts them from the lattice. In turn, the Fermi level is determined by the charge-state occupation statistics of the aggregate point-defect population, in a self-consistent manner.

“Shallow” Extended-Wave-Function Levels (15)

The simplest case is a substitutional impurity with one extra electron or hole beyond that necessary to satisfy local bonding requirements. The electron or hole is donated by, but retains a weak Coulomb attraction to, the impurity. This situation is analogous to that of the hydrogen atom, except that the electron or hole mass is determined by the band structure, and the Coulomb attraction is reduced (screened) by the dielectric constant, of the semiconductor. The energy needed to ionize the electron or hole from the impurity is that of the hydrogen atom, multiplied by the effective mass, divided by the dielectric constant squared.

As discussed in Sections 2.5 and 6.1, effective masses increase, and dielectric constants decrease, with bandgap; hence ionization energies increase roughly as bandgap cubed. Hence, wider-bandgap semiconductors are more difficult to “dope” than narrower-bandgap semiconductors. And, since holes are heavier than electrons, p-type doping is more difficult than n-type doping. Note that ionization energies must be less than $kT \sim 25\text{meV}$ for significant ionization, or “activation,” of donors or acceptors at room temperature. Hence, semiconductors with bandgaps wider than 2.5-3.0eV are difficult to dope n-type, while those with bandgaps wider than 1.0-1.5eV are difficult to dope p-type.

“Deep” Localized-Wave-Function Levels (23)

In some cases, the electron or hole interacts as (or more) strongly with the localized central-cell, as with the delocalized Coulomb, potentials associated with the point defect -- particularly if there are large local strains. Then, chemical shifts, or central-cell corrections, usually (but not always) cause the electron or hole to be more deeply bound than the hydrogenic effective-mass model would predict.

Because these “deep” levels are localized, and interact relatively weakly with delocalized lattice electrons, they change charge states sluggishly, causing slow, thermally activated capacitance transients in Fermi-level-sweeping experiments. Also, because these deep levels are within the gap, recombination of electrons and holes, where one or both reside on a single (or neighboring) point defect, manifests itself as normally-unobserved within-bandgap luminescence.

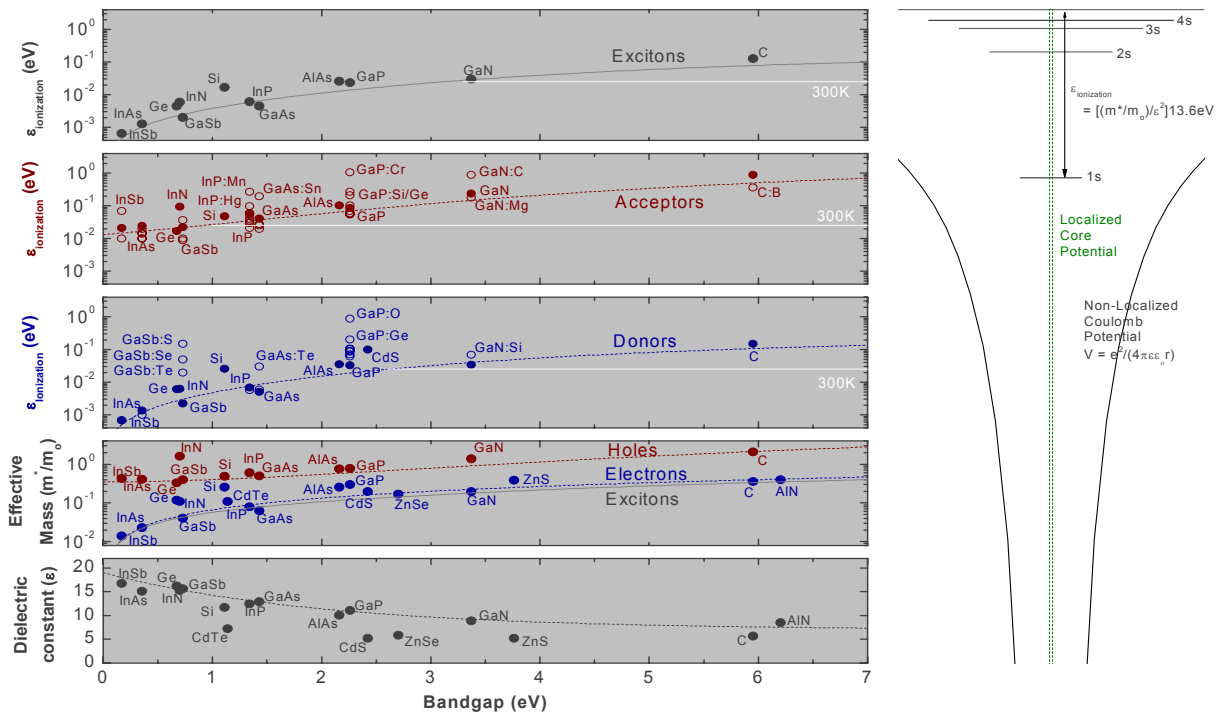
Excitons (22)

Electrons and holes can bind not only to point defects, but to each other. The result is a localized electron-hole pair, or exciton. The ionization energy of excitons is slightly less than that of donors and acceptors, because of its “reduced” effective mass. When an electron and hole pair in an exciton recombine, the energy of the resulting photon is reduced from the band-edge by the exciton ionization energy.

Note that the central-cell potentials that give rise to deep levels can also capture and bind excitons. When an electron-hole pair in such a bound exciton recombine, the photon energy is reduced even further from the band-edge by the binding energy of the exciton to the point defect. A famous example is GaP: N_P , in which excitons are bound to the localized strain field associated with N_P , enabling red and yellow photoluminescence despite a normally low recombination rate associated with indirect-gap GaP.

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1.4 Electrons and Defect Centers (53)

Point Defect Centers (2)

In the simplest cases, point defects don't interact with each other. In more complex cases, they do. These interactions can lead to coupled changes in charge state and local bonding configurations, reminiscent of coupled electron and atomic configurations in molecular spectroscopy. The best-studied examples are the so-called DX and EL2 Centers, and hydrogen passivation of donors and acceptors.

Metastable Centers: DX (16)

DX⁻ Centers occur in many compound semiconductors, rendering them difficult to dope n-type. Originally thought to be complexes between a donor (D) and an unknown (X) point defect site, they are now believed to be associated with donors that accommodate multiple local bonding configurations.

A model for these configurations is illustrated for the case of AlGaAs:Si. In one configuration the Si atom sits on a substitutional Ga site, either not ionized ($d^0 \equiv \text{Si}_{\text{Ga}}^0$), or ionized ($d^+ \equiv \text{Si}_{\text{Ga}}^+$). In another configuration the Si atom has moved downwards, breaking its top As bond, effectively creating an interstitial Si atom combined with a Ga vacancy ($\text{DX}^- \equiv \text{Si}_i\text{V}_{\text{Ga}}^-$). It has a -1 charge state because, in changing configurations, the d^+ donor captures two electrons from the lattice to passivate the two dangling bonds left behind.

For GaAs, the shallow substitutional configurations have the lowest energy, and normal donor behavior is observed. For AlGaAs with >22% Al content, the DX⁻ configuration has the lowest energy, trapping electrons and compensating donors. In the presence of light, however, an electron can be ionized into the conduction band, causing the Si atom to relax "upwards" into its shallow positively-charged substitutional site. The resulting photoconductivity persists until the Si atom thermally relaxes back to its deep negatively-charged interstitial site.

Metastable Centers: EL2 (21)

The EL2 Center in GaAs is a deep donor, 0.82eV below the conduction band. It is responsible for compensating the normal

background of shallow C acceptors, leading to the semi-insulating GaAs so useful for electrical isolation of laterally integrated devices.

A model for its configurations is illustrated for GaAs. It is similar to the DX Center, except that it involves As antisites, rather than donor impurities. In one configuration the As atom sits on a substitutional Ga site, usually doubly ionized ($\text{EL2}^{2+} \equiv \text{As}_{\text{Ga}}^{2+}$). This is the configuration that leads to compensation, through donation of two electrons to shallow (e.g., C) acceptors. In another configuration the As atom has moved downwards, breaking its upper As bond, effectively creating an interstitial As atom combined with a Ga vacancy ($\text{EL2}^0 \equiv \text{As}_i\text{V}_{\text{Ga}}$). It has a neutral charge state because, in changing configurations, the EL2^{2+} double donor captures two electrons from the lattice to passivate the two dangling bonds left behind. This configuration is always metastable, but can be created by photoionization, leading, just as with the DX Center, to persistent photoconductivity.

Hydrogen Complexes and Passivation (14)

H is the most common unintentional element found in semiconductors, because of: its presence in processing environments; its small size and high diffusivity; and its "dangling" bond reactivity.

It passivates shallow donors (and acceptors), by insertion into a donor-lattice (or acceptor-lattice) bond, while either capturing an electron from (or donating an electron to) the lattice to either fill (or empty) the dangling bond left behind. Depassivating H-passivated donors or acceptors can be challenging: the most common example is GaN, for which much effort has expended developing techniques to depassivate H-passivated Mg.

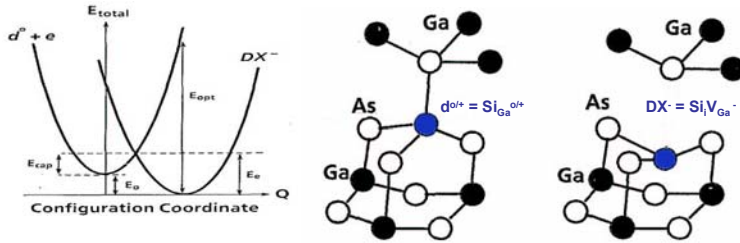
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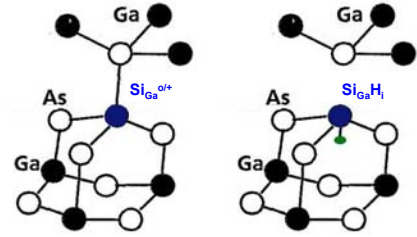
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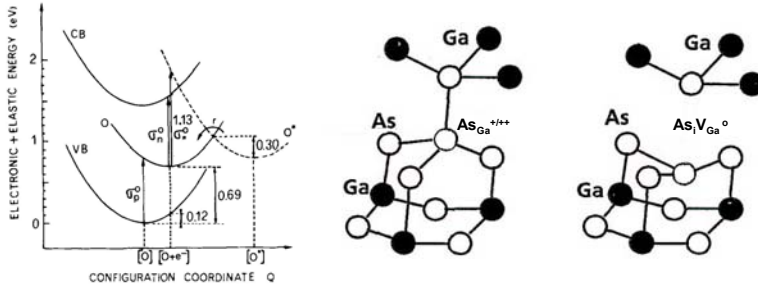


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H + Donor Complex



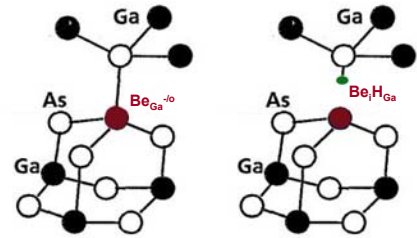
EL2 Center



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1.5 Electron Dynamics (56)

Relaxation Hierarchy (1)

The basis for most device phenomena in compound semiconductors is the response of electrons or holes to external perturbations such as optical or electrical fields. The way electrons and holes are distributed (in phase, momentum, energy and electron band, or space) is shifted by these external perturbations. The magnitude of the shift is determined by a dynamic balance between the magnitude of the perturbation and the rate of the internal scattering processes through which the electron and hole distributions relax back towards thermal equilibrium.

Ultrafast Carrier-Carrier Scattering: Response to Ultrashort Optical Pulses (14)

At the extreme $\sim 10^{18}$ cm⁻³ carrier densities often produced by intense, ultrashort optical pulses, the dominant scattering process is between carriers, on a time scale of the order 10-100 fs.

The scattering events may be elastic, but nevertheless lead to a randomization of the dipole phase relationship between the as-created electron and hole wave functions as well as a broadened momentum distribution. They may also be inelastic, and lead to a thermal (though “hot”) carrier distribution, which subsequently cools slowly to the lattice temperature through interactions with phonons.

Fast Phonon and Defect Scattering: Response to Electric Fields (29)

At less extreme carrier densities, but for carriers accelerated to high energies by high electric fields, the dominant scattering process is with phonons (both acoustic and optical), on a time scale of the order 3-30 ps. At the highest electric fields, electrons scatter from lower-energy-but-higher-mobility Γ valleys into higher-energy-but-lower-mobility L valleys. This causes electron velocities to decrease with increasing electric field, giving rise to negative differential resistance and, in turn, a variety of high-field oscillatory transport phenomena. At slightly lower electric fields, electron velocities are already nearly saturated, due to a combination of optical phonon emission and, if bandgaps are

narrow enough, impact ionization creation of electron-hole pairs.

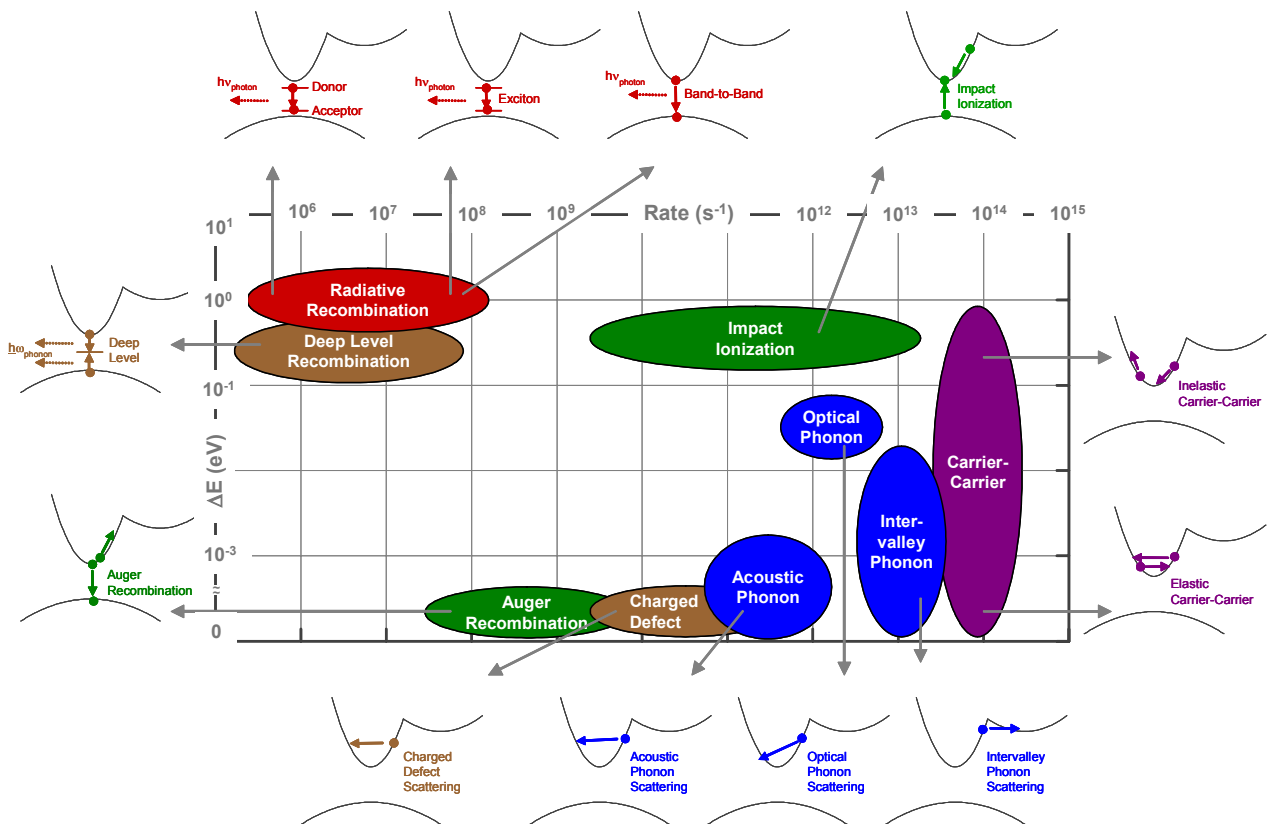
For carriers accelerated by low electric fields, velocities increase linearly with electric field and carrier mobilities are independent of electric field. The dominant scattering processes are from phonons, at room and higher temperatures, as well as from defects of various kinds, at lower temperatures. Ionized donors or acceptors are usually the most important defects in doped material (the Brooks-Herring limit); but compositional fluctuations are also important in ternary and quaternary alloys. In the presence of magnetic fields, additional scattering processes involving carrier magnetic moments may enter in, especially if the material is itself partially magnetic (e.g., InMnAs).

Slow Electron-Hole Recombination: Response to Minority Carrier Injection (12)

In the absence of significant carrier energies, but if both electrons and holes are present, the remaining dynamic process is electron-hole recombination, on a much slower time scale of the order 1-10 ns.

Radiative recombination leads to photons. At higher temperatures, free electrons and holes recombine directly, and the photons are at the bandgap energy. At lower temperatures, electrons and holes pair into excitons before recombining, and the photon energy is reduced by the exciton ionization energy. Also at lower temperatures, electrons and holes on unionized donors and acceptors can recombine, and the photon energy is reduced by the donor and acceptor ionization energies, but increased by the Coulomb attraction energy of the resulting ionized donors and acceptors.

Non-radiative recombination does not lead to photons. In narrow-gap materials, recombination can occur through Auger excitation of third carriers. In wider-gap materials with deep level defects, recombination can occur through sequential electron and hole capture by the deep level defect, accompanied by multiphonon emission or Auger excitation of third carriers.



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2 ELECTRONS AT HETEROJUNCTIONS (228)

One- and Many-Electron Phenomena in Heterojunctions

Quantum well effects are also included, provided only the lowest energy level is involved, since then it is essentially a single heterojunction phenomena – there is no difference between a square or deep triangular well

2.1 Semiconductor-Semiconductor Junctions: Band Offsets (52)

Survey

Band gaps vs band offsets

Absolute band-edge reference energies

Valence band offsets and inferred conduction band offsets (or vice versa)

Bulk vs interface contributions

If bulk dominated, one expects transitivity and commutativity; if interface dominated, one doesn't expect transitivity or commutativity

Perfect Interfaces and Pseudomorphic Films (13)

2.1.0.1 Basic physics

2.1.0.2 Early theories

Electron affinity rule for conduction band referencing (Anderson) – the energy gained by adding an additional electron to an atom or solid

Common anion rule for conduction band referencing plus d-orbital corrections

Natural band lineups using free atom referencing (Harrison)

Frensel-Kroemer model

Neutrality levels (Tersoff)

2.1.0.3 Model solid density functional theories

Basic theory

Spin-orbit splittings

Band edge deformation potentials for strained films

Imperfect Interfaces and Strained Films (6)

2.1.0.4 Interface dipoles

2.1.0.5 Dielectrics

2.1.0.6 Free surfaces

2.1.0.7 Piezoelectric effects

Measurement Techniques and Results (12)

2.1.0.8 XPS and CV measurements

2.1.0.9 Quantum well PLE measurements

2.1.0.10 Absolute measurements of χ

2.1.0.11 Survey of Binary and Alloy Interfaces

InGaAs and InAlAs on InP

InGaP/GaAs

AlAs/GaAs

Antimonides

Nitrides

Schottky Barriers (17)

2.1.0.12 Theory

2.1.0.13 Measurements

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2.2 Semiconductor-Metal Junctions: Schottky Barriers (48)

2.3 Electrons at Heterojunctions (37)

Survey

Type I Heterojunctions (10)

2.3.0.1 Space-charge and depletion layer electric fields and energies

2.3.0.2 Energies in a triangular quantum well

2.3.0.3 Conduction band, valence band

2.3.0.4 Doped heterojunctions

2.3.0.5 Interface states

Perpendicular Transport (8)

2.3.0.6 p-n heterojunctions

2.3.0.7 Majority and minority currents

2.3.0.8 Impact and avalanche ionization

2.3.0.9 Electron-phonon interaction

2.3.0.10 Interface States and Recombination

2.3.0.11 Nonlinear oscillations

Parallel Transport (14)

2.3.0.12 High mobility layers

2.3.0.13 Scattering mechanisms

2.3.0.14 Screening

Type II Heterojunctions (3)

2.3.0.15 Interband tunneling

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2.4 2D Electron Gases (34)

Survey

Emphasis on ground-state electron gases

Excited-state electron gases will be treated in quantum well section

Many Body Physics (11)

Emphasis on 1- and Few-Electron Phenomena. Many-Electron (both 1-component and 2-component) Phenomena (in the extreme case, plasmons) will be in Heterojunctions Chapter, even if they are purely bulk effects. Many electron effects are discussed, but only in the context of creating a one-electron potential (e.g., density functional theory).

And, when the Fermi level becomes very high (near the conduction band) or very low (near the valence band), the conduction or valence bands become densely populated with electrons or holes, causing band-filling and many-body effects that alter and “renormalize” the simple one-electron band structure.

2.4.0.1 Coulomb and Exchange Energies

2.4.0.2 Hubbard Models

2.4.0.3 Density Functional Theory

1-Component Gases: Energies (9)

2.4.0.4 Band-Filling and Renormalization

2.4.0.5 Densities of States

2.4.0.6 Plasmons

1-Component Gases: Dynamics (14)

2.4.0.7 Carrier – Carrier (Hot Carrier Relaxation, Excitons, Damping times)

2.4.0.8 Carrier -- Phonon

2.4.0.9 Carrier – Photon (IR Absorption, Optical Properties, DC screening)

2-Component Gases (4)

2.4.0.10 Electron-Hole and Exciton Droplets

2.4.0.11 Interactions with phonons

2.4.0.12 Interactions with photons

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2.5 2DEGs in Magnetic Fields: Integral QHE (40)

Survey (1)

Are these effects seen in Si?

2D Electrons (4)

2.5.0.1 Landau Levels

2.5.0.2 Filling Factor

2.5.0.3 Densities of States

2.5.0.4 G Factors

2.5.0.5 Properties Periodic in Magnetic Field

2D Electron Magnetotransport: Phenomenology (13)

2.5.0.6 Localized and Delocalized States

2.5.0.7 Disorder and Mobility Edges; Percolation

2.5.0.8 Quantum Hall Effect

2.5.0.9 Resistance standards

2.5.0.10 High Current and Non-Ohmic Transport

2D Electron Magnetotransport: Unified Theories (13)

2.5.0.11 Electron Droplets and Edge States

2.5.0.12 Phase Transformations and Critical Exponents

2.5.0.13 Finite Scaling

2D Electron Miscellaneous Interactions (10)

2.5.0.14 Electron Spin Resonance

2.5.0.15 Magnetoexcitons

2.5.0.16 Magnetopolarons

Laterally Modulated Magnetotransport

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2.6 2DEGs in Extreme Magnetic Fields: Fractional QHE (30)

Survey

Filling Factors

Odd-Denominator Excited States (8)

2.6.0.1 The Standard Picture: Laughlin's Many-Body Wave Function

2.6.0.2 Incompressible Quantum Fluids

2.6.0.3 Fractional Charge States

2.6.0.4 Dissipation and Gaps

2.6.0.5 Density Waves

2.6.0.6 Phonons and Rotons

2.6.0.7 Optical Measurements

High Order and Even-Denominator Excited States (13)

2.6.0.8 Composite Fermions and High-Order Excited States

Mapping onto the integral quantum Hall effect

Edge states

2.6.0.9 Spin Depolarization and Even-Denominator Excited States

Spin and Skyrmions

Quantum Solids (9)

2.6.0.10 Wigner Crystals and Glasses

2.6.0.11 Quantum Solids, Quantum Liquids and Quantum Gases

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3 ELECTRONS IN NANOSTRUCTURES (191)

Chapter 3 describes nanostructures in which electrons are confined in one (quantum wells), two (quantum wires) or three (quantum dots) dimensions

Quantum electron phenomena in 2D, 1D and 0D nanostructures

What is the wavelength of an electron

3.1 Quantum Wells: Electron Energies (51)

Survey

Donors and Acceptors (8)

3.1.0.1 Hydrogenic impurity state energies

3.1.0.2 Wave functions

3.1.0.3 Magnetic Field Effects

Electrons and Holes (10)

3.1.0.4 Energies and Wave Functions in Square and Parabolic Wells

3.1.0.5 Band Alignments

3.1.0.6 Interface Roughness

3.1.0.7 Alloy disorder

3.1.0.8 Occupation statistics

Free Excitons (12)

3.1.0.9 Simple Excitons

3.1.0.10 Excited-State Excitons

3.1.0.11 Exciton Transport and Localization

Bound Excitons (9)

3.1.0.12 Bi-excitons

3.1.0.13 Bound Excitons

At donors and acceptors

At surfaces and interfaces

3.1.0.14 Exciton Condensation

3.1.0.15 Magnetoexcitons

Band Structure Complications (12)

3.1.0.16 Band Non-Parabolicity

3.1.0.17 Valence Band Mixing

3.1.0.18 Strain

3.1.0.19 Exchange Interactions

3.1.0.20 Excitons

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3.2 Quantum Wells: Electron Dynamics (31)

Survey

Electron Dynamics (17)

3.2.0.1 Phonons in Quantum Wells

3.2.0.2 Electron-Phonon Momentum Scattering and Mobilities

3.2.0.3 Electron-Phonon Energy Scattering and Hot Carrier Relaxation

3.2.0.4 Electron-Electron Scattering and Spin Relaxation Dynamics

Exciton Dynamics (9)

3.2.0.5 Binding and unbinding

3.2.0.6 Coherency

3.2.0.7 Spin dynamics

Electron Capture and Escape (5)

3.2.0.8 Thermionic emission

3.2.0.9 Tunneling

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3.3 Quantum Wells: Photons and Electrons (37)

Survey

Optical Absorption and Emission (11)

3.3.0.1 Electron-Hole Creation and Recombination

3.3.0.2 Exciton Creation and Recombination

3.3.0.3 Photon Re-Absorption

3.3.0.4 Many-Body Effects

Electro-Optic Effects (12)

3.3.0.5 Electron and Hole Energies and Wave Functions

3.3.0.6 Quantum-Confined Stark Effect and Electroabsorption

3.3.0.7 Internal Piezoelectric Fields

3.3.0.8 Recombination

3.3.0.9 AC Electro-Optics: Electroreflectance and Photorefectance

Nonlinear and Transient Optical Effects (12)

3.3.0.10 Asymmetric Quantum Wells

3.3.0.11 Optical Stark Effects

3.3.0.12 Excitonic Nonlinearities

3.3.0.13 Hole burning

Inner-Core Articles

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5.2.0.3 Photon-Cavity Modes: Polaritons

5.2.0.4 Rabi oscillations

5.2.0.5 Coupled resonators and Bistability

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Photons and Electrons in Resonators: Strongly Coupled (4)

Photons in Waveguides: Survey

Photons in Waveguides: Linear Effects (2)

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5.2.0.7 Single-Mode and Multi-Mode Waveguides

5.2.0.8 Coupled Waveguides

5.2.0.9 Nonlinear Waveguides

Photons in Waveguides: Nonlinear Effects (4)

Photons in Coupled Waveguides (2)

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5.3 Photons in Periodic Microstructures (30)

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5.3.0.3 Volume gratings

5.3.0.4 Bandgaps

5.3.0.5 Donors and Acceptors

3D Photonic Crystals (12)

5.3.0.6 Vector dispersion curves

5.3.0.7 FCC and Diamond crystals

5.3.0.8 Donors and Acceptors

5.3.0.9 Metallodielectric Photonic Crystals

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5.3.0.10 Localization

5.3.0.11 Nonlinear Transport

Photonic Crystal Resonators and Waveguides (3)

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6 SUBSTRATES AND EPITAXY (216)

Describes the science and technology of how materials are fabricated into nanostructures and microstructures

The fabrication typically occurs in two phases – the epitaxy phase, which builds semiconductor structures vertically in additive processes, and the processing phase, which carves out semiconductor structures horizontally and vertically in subtractive processes (as well as adds other non-semiconductor thin films in additive processes)

(5-6) In Chapters 5-6 I describe the nanofabrication technologies for adding material (epitaxy) and subtracting material (processing). These are the technologies that have enabled the mixing and matching of materials and the fabrication of artificially confined structures. Some of this technology is borrowed from Si semiconductor fabrication, but most of it is unique to compound semiconductors.

Chapter 6 describes epitaxy

Chapter 7 describes processing

6.1 Molecular Beam Epitaxy (43)

Survey (1)

Tools (7)

6.1.0.1 Sources

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Gases

6.1.0.2 Wafer Handling and Positioning

Heating

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6.1.0.3 In Situ Monitoring

RHEED

Pyrometry

Reflectance Difference Spectroscopy

Tools for Studying Surfaces (13)

6.1.0.4 Scanning Tunneling Microscopy

6.1.0.5 RHEED

6.1.0.6 Reflectance Difference Spectroscopy

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6.1.0.7 Growth Conditions

6.1.0.8 Low Temperature Growth

Atomic Layer Epitaxy

Migration-Enhanced Epitaxy

6.1.0.9 Interface Sharpness and Thickness Control

6.1.0.10 Crystallinity

6.1.0.11 Purity

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6.1.0.12 Binary (Al/Ga/In)

6.1.0.13 Binary (N/P/As/Sb)

6.1.0.14 Ternaries and Quaternaries

Strain and lattice latching

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6.2 GaAs Surfaces (48)

Survey (4)

GaAs (001) Surfaces (12)

6.2.0.1 Reconstructions

Bonding

Composition

Geometry and relaxations

Surface states

6.2.0.2 Defects in Reconstructions

Domains

Vacancies

Steps

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GaAs non-(001) Surfaces (13)

6.2.0.3 GaAs (111) Surfaces

6.2.0.4 GaAs (110) Surfaces

Atomistic Mechanisms (7)

6.2.0.5 Chemistry

6.2.0.6 Growth on Reconstructed Surfaces

Growth Modes (11)

6.2.0.7 Adatoms, Steps and Peclet numbers

F-vdM growth

Oscillatory growth; RHEED oscillations

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6.2.0.8 2D Island and Layer Growth: RHEED Oscillations

6.2.0.9 Step-Flow at Higher Temperatures

6.2.0.10 Roughening at Lower Temperatures

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6.3 Non-GaAs Surfaces (33)

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6.3.0.1 Reconstructions

6.3.0.2 Interfaces

6.3.0.3 Polar on Non-Polar Interfaces

Kinetics: Segregation and Trapping (12)

6.3.0.4 Dopants and Impurities

6.3.0.5 Impurities

6.3.0.6 Segregation and trapping

6.3.0.7 Off-stoichiometric growth (LT-GaAs)

6.3.0.8 Lateral segregation -- tilted superlattices

Composition Tailoring (6)

6.3.0.9 Delta Doping

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6.4 Organometallic Vapor Phase Epitaxy (53)

Survey (2)

Fluid Injection and Transport (11)

6.4.0.1 Gas-Mixing Manifolds

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6.4.0.2 Low-Pressure Geometries

CBE

GSMBE

MOMBE

6.4.0.3 High-Pressure Geometries

Horizontal Flow

Vertical Flow

6.4.0.3.1.1 Chemically Reacting Fluid flow

6.4.0.3.1.2 Surface chemical reaction rates

6.4.0.3.1.3 Transport-limited vs reaction-limited regimes

6.4.0.3.1.4 Uniformity vs efficiency

6.4.0.3.1.5 Instabilities: GaN tools

Processes (11)

6.4.0.4 Precursors

MO's

Hydrides

Novel Precursors

6.4.0.5 Temperatures

6.4.0.6 Substrates and Orientations

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6.4.0.7 GaAs

6.4.0.8 InP and Other Alloys

6.4.0.9 In Situ Monitoring

RDS

Advisor

Emissivity corrected pyrometry

X-Ray Scattering

Chemistry Mechanisms (11)

6.4.0.10 Gas Phase Chemistry

6.4.0.11 Surface Reconstructions

6.4.0.12 Surface Phase Chemistry

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6.5 Patterned Surfaces (26)

Survey

Growth on Non-Planar Surfaces (5)

6.5.0.1 Slightly Non-Planar Surfaces: Corrugated and Macrostepped Surfaces

6.5.0.2 Faceted Surfaces

6.5.0.3 Rounded Surfaces

Selective Area Growth (8)

6.5.0.4 Selective Area Epitaxy vs Selective Area Growth

6.5.0.5 OMVPE, MOMBE, CBE

6.5.0.6 Consequences on Mass Transport

6.5.0.7 Shape Evolution

Selective Area Overgrowth: Epitaxial Lateral Overgrowth (6)

6.5.0.8 Vertical vs Lateral Growth Rate Anisotropies

6.5.0.9 Evolution and Filtering of Defects

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7 THIN FILMS (147)

7.1 Crystallography and Defects (37)

Crystallography (4)

The backdrop for all thin film phenomena is crystallography: how atoms are arranged into a lattice. This backdrop helps determine the type, energetics and motions of point, line and planar defects that facilitate thin film growth and processing.

There are hundreds of known crystal structures, with various symmetries and arrangements of atoms. For the simple binary $A^N B^{8-N}$ “octet” semiconductors, however, there are only two major families: the four-fold (tetrahedrally) coordinated diamond/zincblende and wurtzite structures, and the six-and-eight-fold (non-tetrahedrally) coordinated face-centered cubic (FCC), NiAs, NaCl and CsCl structures.

Trends with Polarity and Metallicity (5)

Various physical scales have been used over the years to systematize which compounds favor which crystal structure, including differences between the sizes, valences, and electronegativities of the constituent atoms. Here, we use, following Harrison, the simple (and imperfect) physical scales defined in Section 2.1. First is the polarity of the bonds between the atoms in the lattice -- the tendency of electrons to be transferred from cation to anion, and for the bonding to be partly electrostatic. Second is the metallicity of the bonds -- the tendency of the gap between the bonding (valence) and anti-bonding (conduction) bands, and the energy necessary for an electron to freely wander through the solid, to disappear.

On the one hand, for highly covalent bonding, a tetrahedral coordination consistent with the four sp^3 hybrid bonds between atoms is favored. These are the diamond/zincblende and wurtzite structures in the center of the diagram.

On the other hand, for highly metallic or polar bonding, the angular rigidity associated with a tetrahedral coordination decreases, and more-highly-coordinated more-closely-packed structures are favored. These are: the twelve-fold-coordinated face-centered-cubic (FCC) structure at the top of the diagram; and the six-fold-coordinated NiAs/NaCl and eight-fold-coordinated CsCl structures at the bottom of the diagram.

Zincblende and Wurtzite (3)

The most important crystal structures for the compound III-V semiconductors are the tetrahedrally coordinated ones. Of the three most important compound semiconductor materials, two (GaAs and InP) are zincblende and one (GaN) is wurtzite. The fundamental units of construction for both structures can be thought of as the pair of tetrahedra connected by the red bonds in the right figures.

In zincblende, the two tetrahedra are in a “staggered” orientation where the third-nearest-neighbor cations and anions are rotated away from each other. In wurtzite, the two tetrahedra are in an “eclipsed” orientation where the third-nearest-neighbor cations and anions are rotated towards each other.

Hence, higher-polarity compounds, in order to enhance their third-nearest-neighbor cation-anion electrostatic attraction, tend to crystallize in the wurtzite structure. This is countered by the trend for higher-metallicity compounds, in which electrostatic interactions are better screened, to crystallize in the zincblende structure.

Polytypism (6)

At the border between the zincblende and wurtzite boundary in polarity and metallicity, the lattices are marginally one structure or the other. Then, both structures are often observed (polytypism). For example, GaN, normally wurtzite if grown on a substrate with hexagonal symmetry, can also be zincblende if grown on a substrate with cubic symmetry; and likewise for many of the II-VI compounds near the boundary.

Line Defects

7.1.0.1 Edge and screw dislocations

7.1.0.2 Misfit and threading dislocations

Point Defects

7.1.0.3 Intrinsic: Vacancies, Interstitials, Anti-Site

7.1.0.4 Extrinsic: Isovalent, Non-Isovalent, Multi-Charge

Point Defect Complexes

7.1.0.5 Pairs (GaP:N)

7.1.0.6 As precipitates

Thermodynamics

7.1.0.7 Chemical potential of off-stoichiometry defects will depend on III/V stoichiometry of the lattice, and the difference between III and V chemical potentials

7.1.0.8 Electrochemical potential of charged defects will depend on Fermi energy and the difference between the electron and hole electrochemical potentials (will be discussed in more detail later)

7.1.0.9 Trends in Thermodynamics: Across defect types, Across materials families

Defect Complexes (2)

7.1.0.10 Clusters of Point Defects

As precipitation

Transition to metallic behavior

Space charge fields

Anti-percolation and transition to semi-insulating behavior

7.1.0.11 Line Defects

Dislocations (active and passive)

Recombination

Space Charge Fields

7.1.0.12 Surfaces

Dangling bonds

Deep levels and Fermi level pinning

Recombination

Inner-Core Articles

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7.2.0.3 Composition Modulation

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Dislocations Energies

7.2.0.6 Dislocation Dynamics

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7.2.0.7 Dislocation Filtering

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Thick Growth

Inner-Core Articles

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7.3.0.3 Epitaxial Constraints

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Epitaxially constrained ternaries and quaternaries

7.3.0.4 Unstrained binaries, ternaries, quaternaries

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Epitaxial Lattices (5)

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7.4.0.5 MBE vs OMVPE

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7.5.0.8 Dislocation filtering through thick growth

7.5.0.9 Residual line and planar defects

7.5.0.10 Strain effects

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8.1.0.4 Impurity Diffusion

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8.1.0.8 Precipitation at Defects

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8.1.0.9 Ion-Beam Mixing

8.1.0.10 Implant Enhanced Diffusion

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8.2 Surface Processing (49)

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8.2.0.9 Trends in Reactivities

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Crystallographic selectivity

8.2.0.10 Deep Etching

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8.2.0.13 Electrochemical Etching

8.2.0.14 Electrochemical Deposition

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8.3 Thin Films (32)

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8.3.0.4 Diagnostics

8.3.0.5 Dielectrics, Metals

8.3.0.6 Trade-offs and Trends in Uniformity, Rate, Flexibility, Composition, Microstructure

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8.3.0.12 Trends with Bandgap and Materials

8.3.0.13 Superconducting Contacts

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8.4 Lithography and Substrate Engineering (31)

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8.4.0.2 Photomasks

8.4.0.3 Contact and near-contact mask alignment

8.4.0.4 Projection lithography

8.4.0.5 Near-field holography

8.4.0.6 Direct atom manipulation

8.4.0.7 E-Beam Lithography

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8.4.0.8 Cleaning

8.4.0.9 Cleaving

8.4.0.10 Bonding

8.4.0.11 Lift-Off

8.4.0.12 CMP

8.4.0.13 Compliant Substrates

8.4.0.14 HVPE

8.4.0.15 Plating

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9 ELECTRONICS (75)

Survey of Electronics (2)

Describes the technology and applications of devices which make use of bandgap nanoscience in compound semiconductor materials

These devices are categorized according to whether they are purely electronic, or optoelectronic

(7-9) In Chapters 7-9 I describe how all of these materials, nanoscience and nanotechnology building blocks result in powerful new electronic and photonic devices. I also describe the markets and economics associated with these devices – why they are useful today, and how they can improve to become more useful tomorrow.

Chapter 8 describes electronic devices

Chapters 9 and 10 describe optoelectronic devices – first those in which light propagates “in the plane” of the wafer, and second those in which light propagates “out of the plane” of the wafer

Chapter 11 describes the applications and markets for these devices

9.1 MESFETs, MISFETs, HEMT's (41)

Survey

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9.1.0.1 Enhancement and Depletion Mode FETs

9.1.0.2 N-channel and P-channel FETs

9.1.0.3 MESFETs vs MISFETs

9.1.0.4 Ballistic transport

9.1.0.5 Vertical FETs

Fabrication (7)

9.1.0.6 Self-alignment

9.1.0.7 Ion implantation

9.1.0.8 Non-epi vs epi devices

9.1.0.9 Epi tolerances

Performance scaling (4)

9.1.0.10 Speed (small signal for analog, large signal for digital)

9.1.0.11 Power

9.1.0.12 Noise for digital

9.1.0.13 Linearity for analog

9.1.0.14 Integrability

HEMTs (8)

Modulation doping

GaAs vs InP vs InAs vs InSb

Speed (small signal for analog, large signal for digital)

Power

Noise for digital

Linearity for analog

Integrability

Fabrication (5)

9.1.0.15 Delta doping

9.1.0.16 Insulating buffers

9.1.0.17 Selective etch stops

9.1.0.18 Self-alignment

9.1.0.19 Epi tolerances

Magnetoresistors (1)

9.1.0.20 Hall effect devices

Nanodevices

9.1.0.21 Ballistic Devices

9.1.0.22 Single-Electron Devices

9.1.0.23 Quantum Interference Devices

Inner-Core Articles

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9.2 Diodes, Triodes, Mixers, HBTs (35)

Survey

Diodes, Triodes, Mixers (4)

9.2.0.1 Radiometric detectors

9.2.0.2 Gunn effect and Gunn diodes

Oscillatory phenomena in which moving domains of higher electric field and charge density:

nucleate (usually at the cathode),

drift at the peak electron saturation velocity across a sample,

are sharpened and stabilized as they drift by negative differential resistance which causes electron bunching,

then annihilate at the anode

Typical saturation velocities are $1e7\text{cm/s}$ and typical sample lengths are 10microns , so typical oscillation frequencies are 10GHz , in the microwave range

The key is negative differential resistance, which can occur in bulk materials (the effect was first observed in n-GaAs and in tunneling (Esaki) and resonant tunneling diodes

HBTs: Basic Geometry and Performance Scaling (7)

9.2.0.3 Homojunction vs heterojunction devices

9.2.0.4 GaAs vs InP vs GaN

9.2.0.5 Surface recombination

9.2.0.6 Speed (small signal for analog, large signal for digital)

9.2.0.7 Power

9.2.0.8 Noise for digital

9.2.0.9 Linearity for analog

9.2.0.10 Integrability

HBTs: Advanced Fabrication (4)

9.2.0.11 HBTs: Fabrication

9.2.0.12 Graded layers

9.2.0.13 Heavily doped bases

9.2.0.14 Surface passivated structures

Nanodevices and Antennas

9.2.0.15 Tunneling

9.2.0.16 Resonant Tunneling

9.2.0.17 Field emitters and vacuum electronics

9.2.0.18 Antennas

Inner-Core Articles

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10 IN-PLANE OPTOELECTRONICS (168)

Survey of In-Plane Optoelectronics (0)

Mostly edge-emitting lasers

10.1 Broad Stripe Double Heterostructure Lasers (30)

Survey

Basic Geometry, Equations and Performance (10)

10.1.0.1 Spontaneous and stimulated emission

10.1.0.2 Gain and loss

10.1.0.3 Transparency

10.1.0.4 Below threshold and above threshold characteristics

10.1.0.5 Confinement factor

10.1.0.6 Vertical Optical Cavity Engineering

Separate Confinement

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10.1.0.7 Doped vs undoped active regions

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10.1.0.10 InP-based (InGaAsP, InAlGaAs)

10.1.0.11 GaN-based

10.1.0.12 Aging

10.1.0.13 Limits to Performance

Reliability -- Facet Damage

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10.2 Gain and Bandwidth Engineering (32)

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Quantum Wells (18)

10.2.0.1 Optimal number of wells

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10.2.0.3 Semi-empirical gain vs n vs j equations

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10.2.0.11 Electrons and Holes (Transport)

10.2.0.12 Photons

10.2.0.13 Index Changes and Chirping

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10.3 Transverse Mode and Polarization Engineering (18)

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10.3.0.4 Photocarrier and thermal lensing

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10.3.0.6 Buried Heterostructures

10.3.0.7 Channeled substrate

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10.3.0.9 Buried oxide

Laterally Coupled Arrays (3)

10.3.0.10 Symmetric supermodes

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10.4 Longitudinal Mode and Noise Engineering (34)

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10.4.0.2 Composite cavities

10.4.0.3 Temperature issues

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10.4.0.4 Distributed feedback (DFBs, DBRs)

10.4.0.5 Coupled modes

10.4.0.6 Homogenous and inhomogeneous gain

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10.4.0.8 Phase locking

10.4.0.9 Squeezed States; Chaos

10.4.0.10 Intermodulation and harmonic distortion

10.4.0.11 External optical feedback

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10.5 Hybrid and Integrated Devices (26)

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10.5.0.14 Waveguides and bends

10.5.0.15 Filters and waveguide-coupling modulators

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11 OUT-OF-PLANE OPTOELECTRONICS

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11.2.0.2 Texturing

11.2.0.3 Transparent substrates

11.2.0.4 Transparent electrodes

11.2.0.5 Wafer bonding

11.2.0.6 Resonant-cavity LEDs

11.2.0.7 Superluminescent LEDs

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11.3 VCSELs (28)

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11.3.0.1 Equations

11.3.0.2 Cavity length

11.3.0.3 DBRs

11.3.0.4 Active regions

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11.3.0.8 Polarization

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11.3.0.10 Current spreading and crowding

11.3.0.11 Speed

11.3.0.12 Reliability

11.3.0.13 Noise

InP and GaN based VCSELs

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11.4 Detectors and Solar Cells (25)

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11.4.0.1 Figures of merit – Detectivity, Noise-equivalent power, Speed

11.4.0.2 PIN Photodiodes

11.4.0.3 Photovoltaic IR detectors

11.4.0.4 Fabrication

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11.4.0.7 Figures of merit – Efficiency, Cost

11.4.0.8 Fabrication

Multijunction Solar Cells (5)

Light Input Engineering (1)

11.4.0.9 Internal and external efficiencies

11.4.0.10 Texturing

Photoelectrochemical Solar Cells (5)

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11.5 Modulators, Gates and Hybrid Devices (24)

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Light Valves and Modulators (7)

11.5.0.1 Schottky diodes

11.5.0.2 Saturable absorbers

11.5.0.3 Photobleaching and holographic memories

Bistable Devices (14)

11.5.0.4 Excitons and Etalons

11.5.0.5 SEEDs

Hybrid Devices (3)

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12 APPLICATIONS AND MARKETS (11,81)

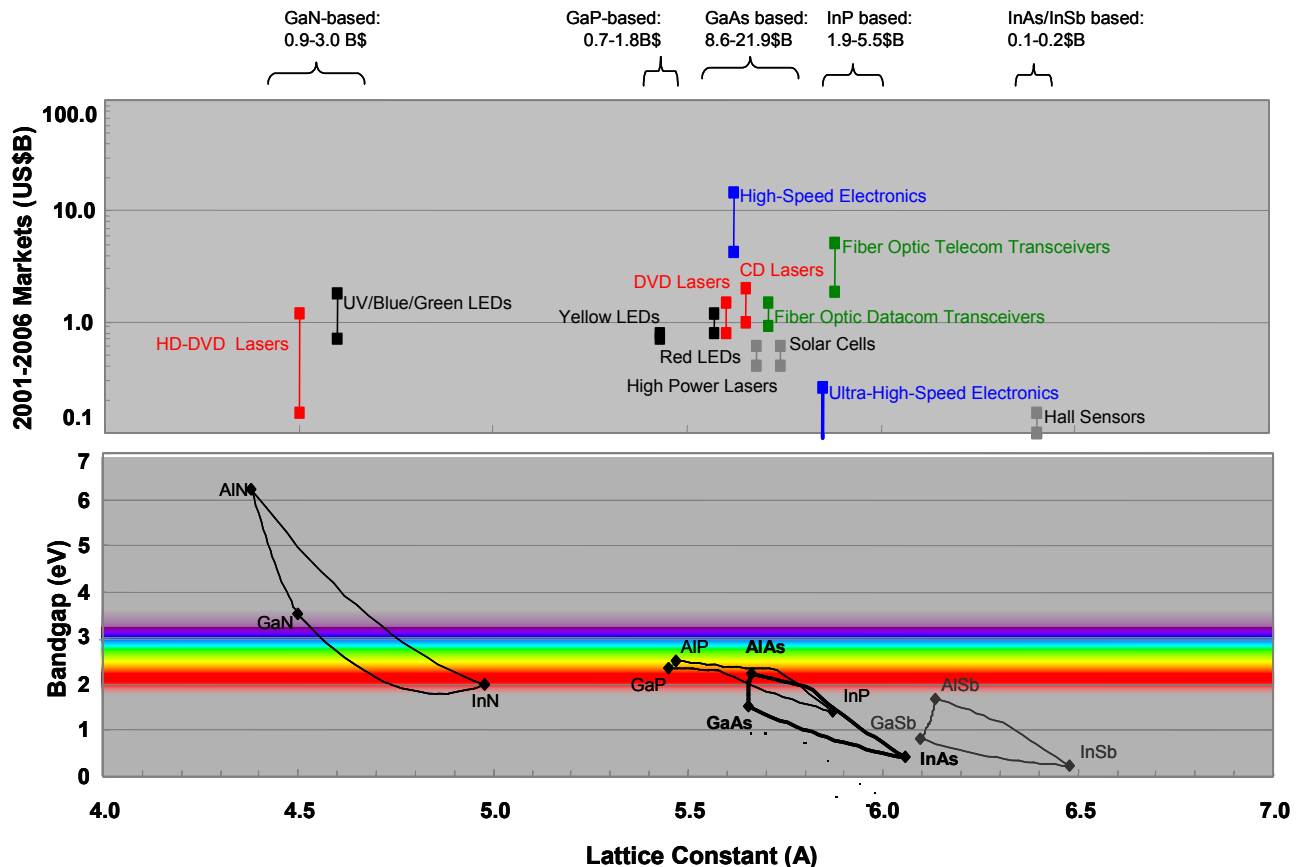
Materials Families

Although the compound III-V semiconductors are a subset of the universe of simple semiconductors, they are a large and rich subset. In fact, these semiconductors form a number of alloy families, within which there is considerable freedom for one of the most crucial features of the compound III-V semiconductors: composition engineering. As composition is engineered, both lattice constant and bandgap are engineered, and devices may be layered with a strain and bandgap profile designed to optimize particular properties.

Sb's, As's, P's, N's

The most important alloy families are the so-called "mixed column III" alloys, where the "cation" sites in the lattice are an alloy of column III elements, while the "anion" sites are a single column V element. From largest to smallest lattice constant, the III-III-III-V alloy families, and their preferred near-lattice-matched substrates, are: (AlGaIn)Sb on InSb or GaSb ; (AlGaIn)As on GaAs, InP or InAs; (AlGaIn)P on GaAs or GaP; and (AlGaIn)N on Al₂O₃, SiC or ZnO.

In principle, there are also "mixed column V" III-V-V-V alloys families, such as Al(PaSb), Ga(PAsSb) and In(PAsSb), and "mixed columns III and V" III-III-V-V alloys families, such as (GaIn)(AsSb), (GaIn)(PAs), and (GaIn)(NP). In practice, composition in V-V alloys is sufficiently difficult to control that the only family of importance is (AlGaIn)(PAs) on InP, because it is the only family that spans the 1.3-1.5 μm wavelength zero-dispersion and zero-absorption window in optical fibers for telecommunications.



Chip Application Families

Each of the III-V alloy families has a number of chip application families, determined by their unique ranges of bandgaps and other properties. These applications are represented by the bars in the Facing Figure. The horizontal position of the bars corresponds to the substrates and materials family in the bottom Figure that the chips are fabricated from. The bottom of each bar represents the 2001 market size for those chips; the top of each bar represents the projected 2006 market size; and since the plot is a log plot, the length of the bars indicates the percentage market size growth rates.

Top 4 Chip Applications

There are 4 “big” applications for compound III-V semiconductor chips.

The first is high-speed electronics: the analog integrated circuits used as preamplifiers and power amplifiers for wireless RF and microwave communications, and the high-speed digital integrated circuits used to drive fiber-optic transceivers. These electronic chips are based mostly on GaAs substrates and the AlGaInAs materials family.

The second is fiber-optics: the discrete or integrated lasers, modulators, amplifiers, switches and detectors used for sending and receiving optical signals through optical fibers. These optical chips are based mostly on InP substrates and the (AlGaIn)(PAs) materials family.

The third is optical storage: the (AlGaIn)As-based infrared lasers used for CDs, the GaAs and AlGaInP-based red lasers used for DVDs, and the GaN-based purple lasers that will soon be used for high-definition DVDs.

The fourth is solid-state lighting: the (AlGaIn)P-based red LEDs, and the GaN-based green, blue and UV LEDs that are used for power signaling and someday for general white lighting.

All Chip Applications

All together, the 2001 compound III-V semiconductor chip market was roughly 12 US\$B, and the 2006 projected market is roughly 32 US\$B, a compound annual growth rate of roughly 20%. Indeed, this chip market is now approaching 10% of the 2001 Si chip market of roughly 150 US\$B.

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12.1 Wireless Communications (7)

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GaAs vs InP vs SiGe

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12.1.0.1 Preamplifiers

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12.1.0.2 RF Output Amplifiers

12.1.0.3 Dual Mode (Analog and Digital)

Microwave Systems and Radars (2)

12.1.0.4 Si and ceramic packaging

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12.2 Optical Communications (20)

Survey

12.2.0.1 Bandwidth – Distance Chart

WAN – Long-Haul

MAN – Metro

LAN – Campus

12.2.0.2 Dispersion – Wavelength – Linewidth Chart

12.2.0.3 Transverse vs Longitudinal Mode Chart

12.2.0.4 System noise, etc considerations on laser power, detector sensitivity, fiber or free-space loss, etc

12.2.0.5 Wavelength considerations

12.2.0.6 Materials considerations

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12.2.0.7 Multimode and Singlemode fibers

12.2.0.8 Coupling to fiber and spot size converters

12.2.0.9 Active alignment to fibers

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12.2.0.10 Temperature stabilization

12.2.0.11 Amplitude stabilization

12.2.0.12 FP vs DFBs vs VCSELs

12.2.0.13 Wavelength stabilization

12.2.0.14 Reliability

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12.2.0.15 WDM Transmitters

12.2.0.16 Fiber Amplifiers

EDFAs

Raman Amplifiers

12.2.0.17 Switches, Amplifiers, Receivers

SOAs

12.2.0.18 Drive Electronics

GaAs vs SiGe vs InP

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12.3 Energy Conversion, Imaging, Sensing (10)

Survey

Position Sensing and Scanning (3)

12.3.0.1 Survey

12.3.0.2 Bar Code Scanners

12.3.0.3 CD Players and Writers

12.3.0.4 DVD Players and Writers

12.3.0.5 UDVD

Energy Conversion (2)

12.3.0.6 Survey

12.3.0.7 Terrestrial PV

Efficiency – Cost Considerations

12.3.0.8 Space PV

Weight -- Efficiency – Cost Considerations

Spectroscopy (2)

Imaging (3)

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12.4 Solid State Lighting (11)

Survey

Signaling (3)

12.4.0.1 Color and human eye sensitivity

12.4.0.2 Wavelength considerations

12.4.0.3 Brightness considerations

12.4.0.4 Efficiency considerations

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12.4.0.5 White light and color rendering index

12.4.0.6 Energy efficiency

12.4.0.7 Multi-color direct approach

12.4.0.8 Phosphor indirect approach

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12.5 Materials Processing (14)

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Optical Storage (2)

Printing (4)

Diode-Pumped Solid-State Lasers (13)

Medicine and Cosmetics (1)

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12.6 Data Storage (5)

13 INNER-CORE REFERENCES

Core and Inner-Core Articles and Patents

The science and technology of the world of III-V compound semiconductors is captured in large part by its literature – roughly 37,500 journal articles published, and 7,500 U.S. patents issued, in the past 25 years or so. Of these, those that have been most influential have been those that have been cited most.

As discussed in the Preface, we have created two databases of these most-influential articles and patents. Our core database contains roughly 1500 journal articles that have been cited 100 or more times, and roughly 300 U.S. patents that have been cited 20 or more times. Our inner-core database contains roughly 400 journal articles that have been cited 200 or more times, and roughly 80 U.S. patents that have been cited 40 or more times.

In this Chapter, we list the inner-core journal articles and patents, both alphabetically by author in Sections 13.1 and 13.2, as well as in decreasing order by citation count in Sections 13.3 and 13.4. In all of these Sections, the header number associated with each reference is its citation count as of the 2003-2004 time frame. Note that the citation counts only represent a snapshot in time. Citations, especially for the more recently published or issued journal articles and patents, are increasing rapidly.

Citation Statistics and Selectivity

To get an idea of the selectivity of our core and inner-core databases, we can make a few approximations regarding the statistical distribution of journal articles and patents. The average number, c_{avg} , of citations of journal articles by other journal articles is approximately 30, and of U.S. patents by other U.S. patents approximately 6. The fractional number of journal articles and U.S. patents that has been cited c times is distributed (very) roughly exponentially, $n(c)/N = (1/c_{\text{avg}}) \exp(-c/c_{\text{avg}})$.

Hence, journal articles that have been cited more than 100 times represent (very) roughly $\exp(-100/30)$, or 4%, of all journal articles. U.S. patents

that have been cited more than 20 times represent (very) roughly $\exp(-20/6)$, or 4%, of all U.S. patents.

Likewise, journal articles that have been cited more than 200 times represent (very) roughly $\exp(-200/30)$, or 0.15%, of all journal articles. U.S. patents that have been cited more than 20 times represent (very) roughly $\exp(-40/6)$, or 0.15%, of all U.S. patents.

The ratio between numbers of journal articles and patents in the core database, $1500/300=5$, roughly represents the ratio between the sizes of the overall journal article and U.S. patent literatures. The ratio is also approximately equal to that between the average numbers of journal article and patent citations, $30/6=5$.

Science and Technology

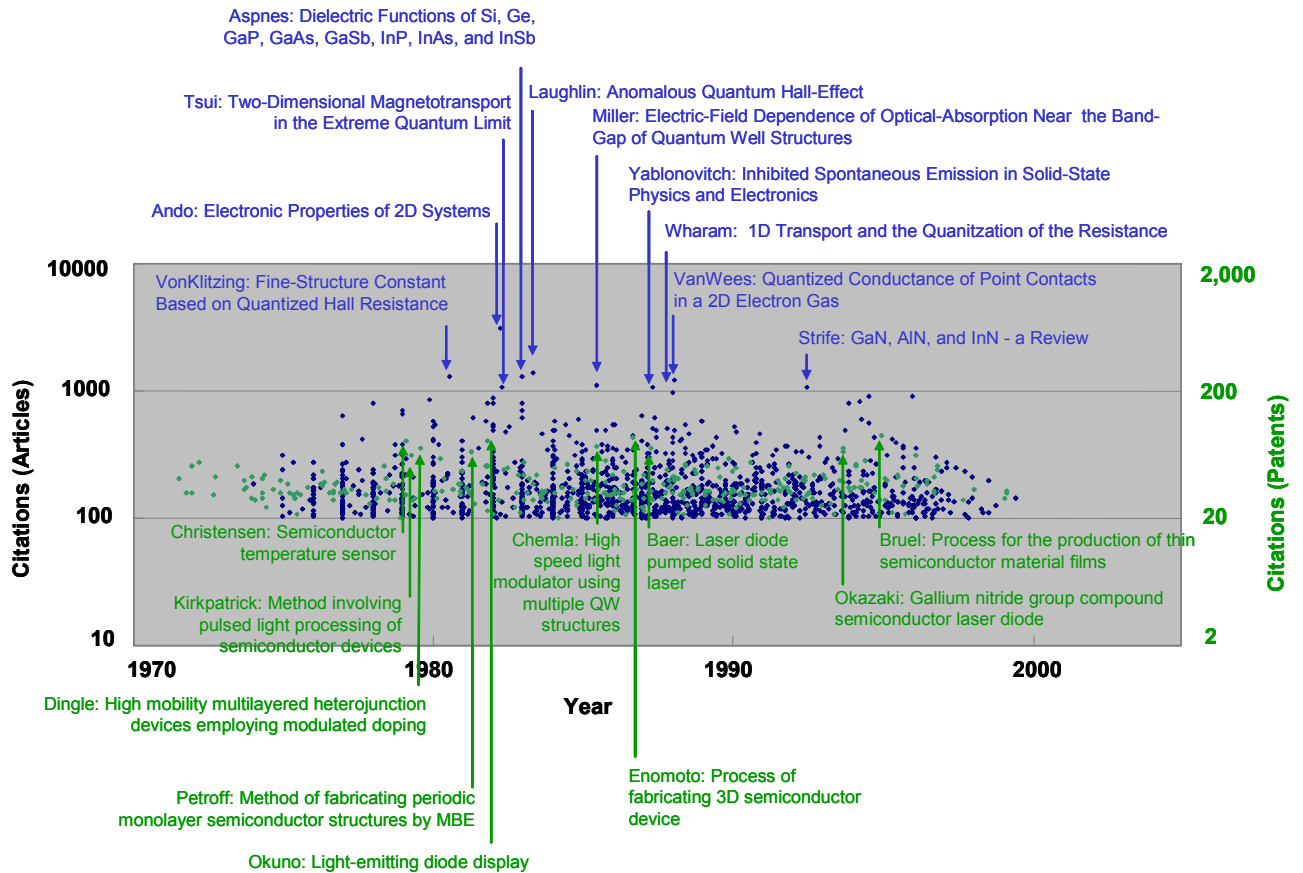
By including both journal articles and patents in our core database, the hope is to cover the science *and* technology associated with the world of compound III-V semiconductors.

Sometimes, that science and technology have been closely interconnected – e.g., the physics of quantum wells and the engineering of quantum-well gain regions in semiconductor lasers. Sometimes, even in areas that superficially have much in common, they have progressed somewhat separately – e.g., the physics of 2D electron gases in high magnetic fields and the engineering of high-electron-mobility transistors.

Someday, it may be interesting, from a “sociology of science” perspective, to understand better the differences between these two and other examples. Hopefully, this guidebook can provide some of the source material for such a study.

The 10 Most-Highly-Cited Articles

Our core database of these highly cited journal articles is plotted in the Facing Figure. The most highly-cited 10 articles, each with more than 900 citations, are listed in blue. Six of them are related to the physics of 2-dimensional electron gases; two are related to the optical properties of bulk and periodically nanotextured materials; one is related to the physics of optoelectronic switching; and one is a



review of the most-recently-developed compound III-V semiconductor materials family, AlGaInN.

The 10 Most-Highly-Cited Patents

Our core database of these highly cited U.S. patents is plotted in the Facing Figure. The most highly-cited 10 U.S. patents, each with more than 60

citations, are listed in green. Five of them are related to fabrication techniques – epitaxy, processing or substrate engineering; two of them are related to designs for optoelectronic devices; and three of them are related to applications of particular device designs.

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