

共价键模型

原子轨道

电子的量子数

$n = 1, 2, 3, \dots$, principal quantum number 主量子数, 描述电子绕核运动的能量或电子的能级

$l = n-1, n-2, \dots, 0$, azimuthal quantum number 角量子数 描述电子绕核运动轨迹(电子云)的形状

$|m| = l, l-1, \dots, 0$, magnetic quantum number 磁量子数 描述电子云方向或电子的磁矩

$s = \pm \frac{1}{2}$, 电子的自旋量子数

每组量子数决定了电子的一种量子态。

泡利不相容原理: 任意给定系统中, 不可能有两个电子处于同一个量子态, 即四个量子数不能完全相等。

n	l	m	s	容纳电子数	轨道
1	0	0	$\pm \frac{1}{2}$	2	1s 2
2	0	0	$\pm \frac{1}{2}$	2	2s
2	1	0, ± 1	$\pm \frac{1}{2}$	6	2p } 8

轨道杂化

考虑多核外电子的原子, 以硅原子(14)为例

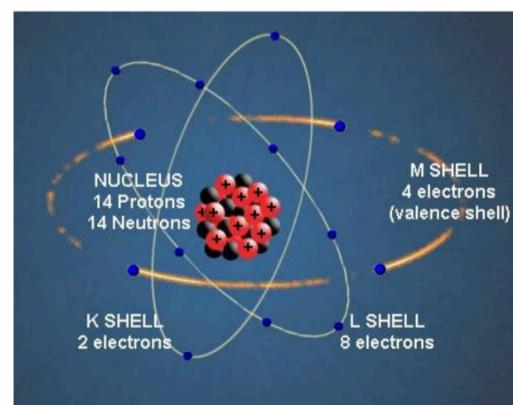
➤ 14 electrons occupying the first 3 energy levels:

- 1s, 2s, 2p orbitals filled by 10 electrons
- 3s, 3p orbitals filled by 4 electrons

To minimize the overall energy, the 3s and 3p orbitals

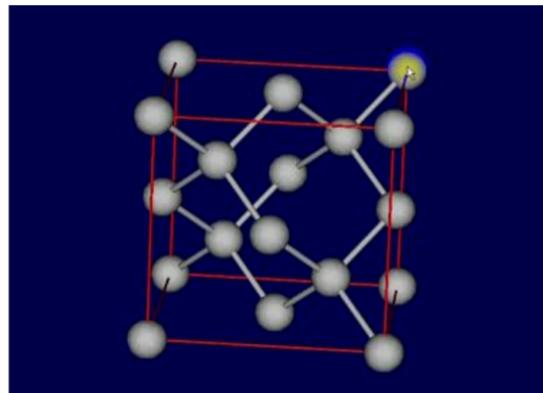
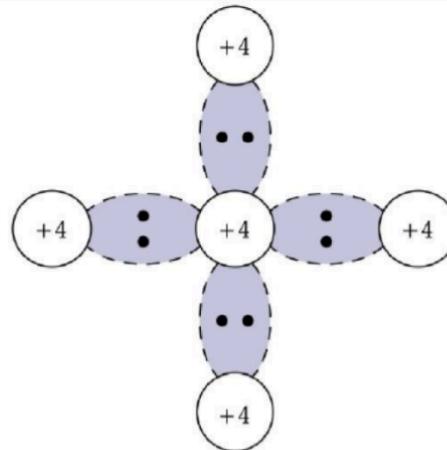
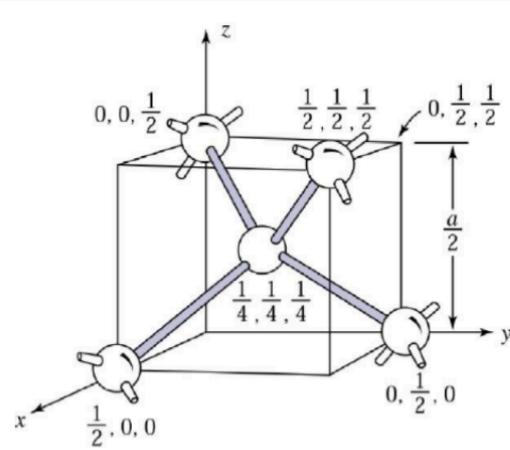
杂化 hybridize to form 4 tetrahedral (正四面体形) 3sp orbitals

Each has one electron and
is capable of forming a bond
with a neighboring atom

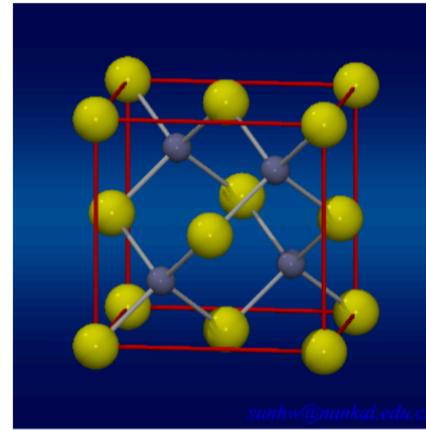


4个sp杂化轨道, 每个杂化轨道同样可以容纳两个电子。对于硅原子, 半填充时能量最低。

因此四个sp轨道都能成键，此键即为：共价键(Covalent Bonding)



Diamond Lattice: Si, Ge



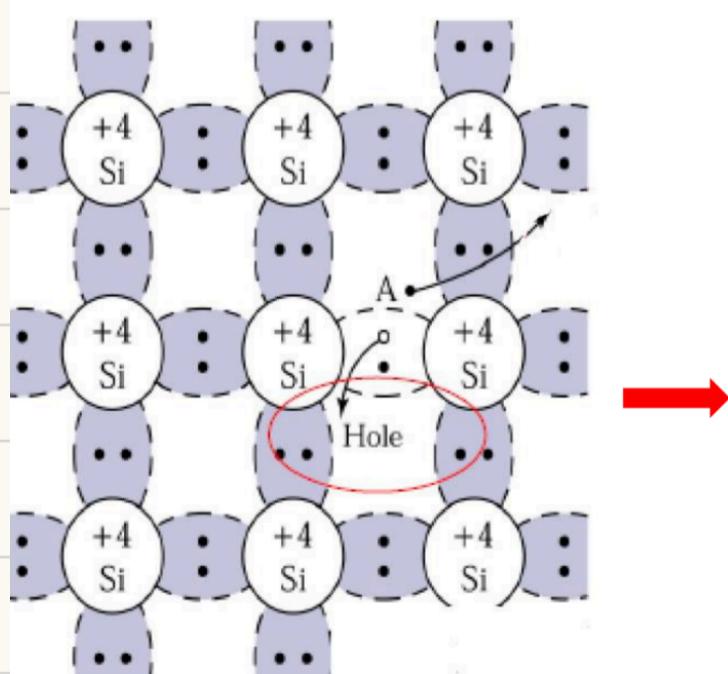
Zincblende Lattice: GaAs, InP

When an electron breaks loose and becomes a conduction electron, a **hole** (空穴) is also created.

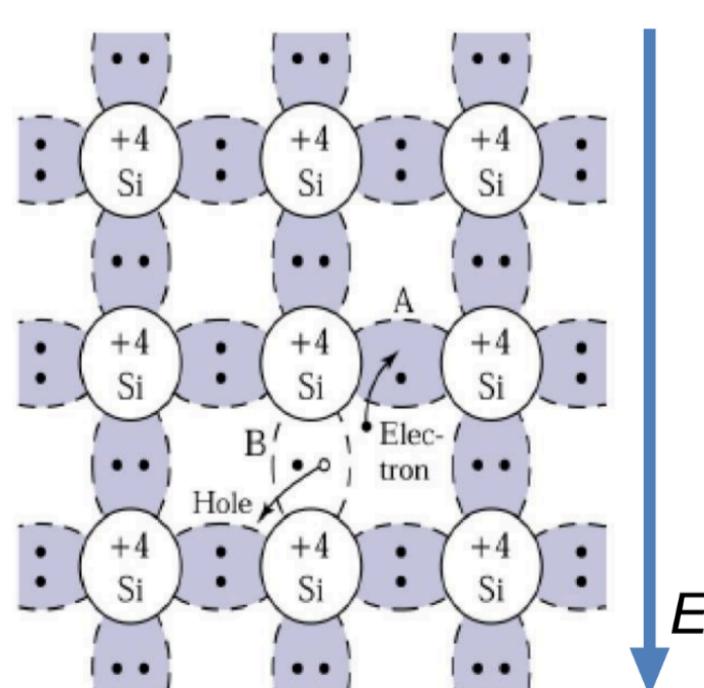
常见载流子：电子和空穴

载流子的移动

可视化：空穴移动



Broken bond at position A,
resulting in a conduction
electron and a hole



Another electron moves from position
B to half-filled bond at position A,
leaving a hole at position B.

本征半导体: Intrinsic Semiconductor, 无掺杂的纯净半导体

本征载流子浓度: Intrinsic Carrier Concentration 本征半导体中的载流子浓度

符号定义

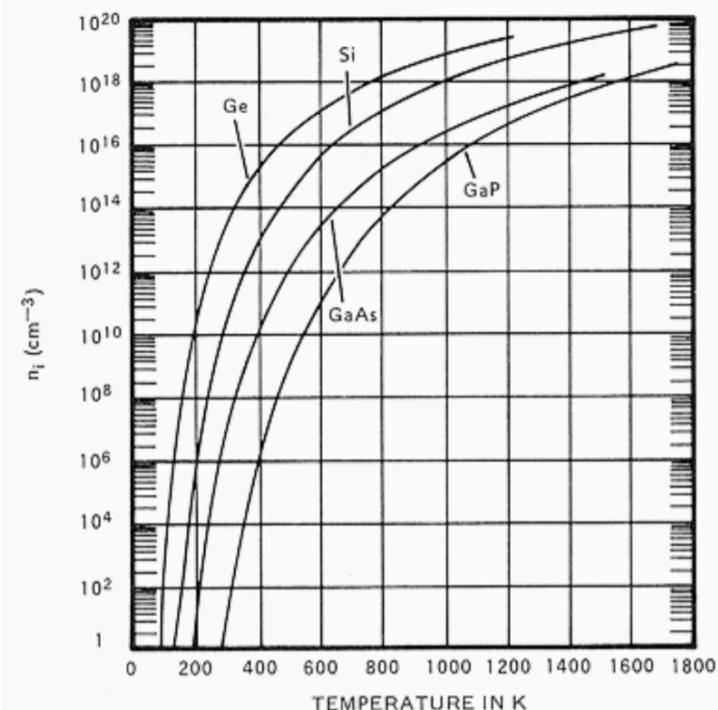
negative: 电子
positive: 空穴

$n \equiv$ number of electrons/cm³

$p \equiv$ number of holes/cm³

$n_i \equiv$ intrinsic carrier concentration

In a pure semiconductor, $n = p = n_i$



本征载流子浓度---温度关系

- Some information at 300K

Si density: 5×10^{22} atoms/cm⁻³

Si: $n_i \approx 10^{10} \text{ cm}^{-3}$

Ge: $n_i \approx 2 \times 10^{13} \text{ cm}^{-3}$

GaAs: $n_i \approx 2 \times 10^6 \text{ cm}^{-3}$

改变载流子浓度的方法

1. by changing the temperature
2. by adding special impurity atoms (dopants)
3. by applying an electric field
4. by irradiation

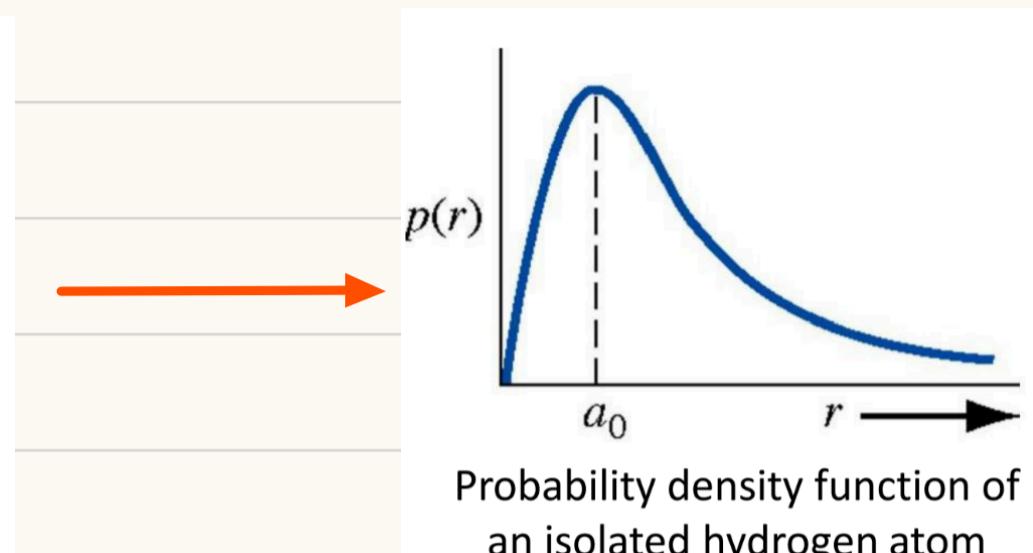
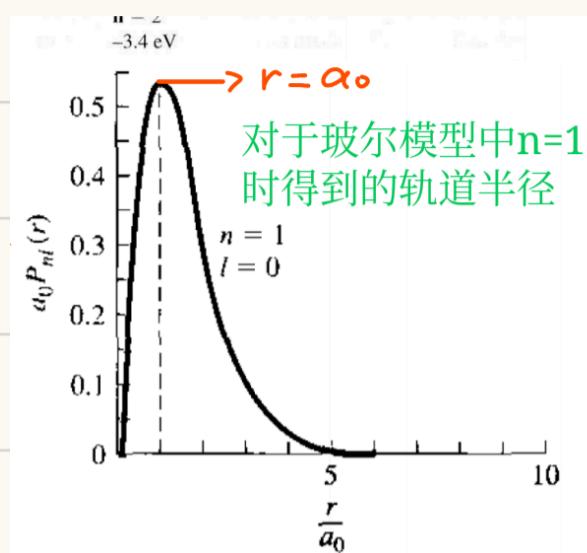
通过添加特殊杂质原子（掺杂剂）

光照

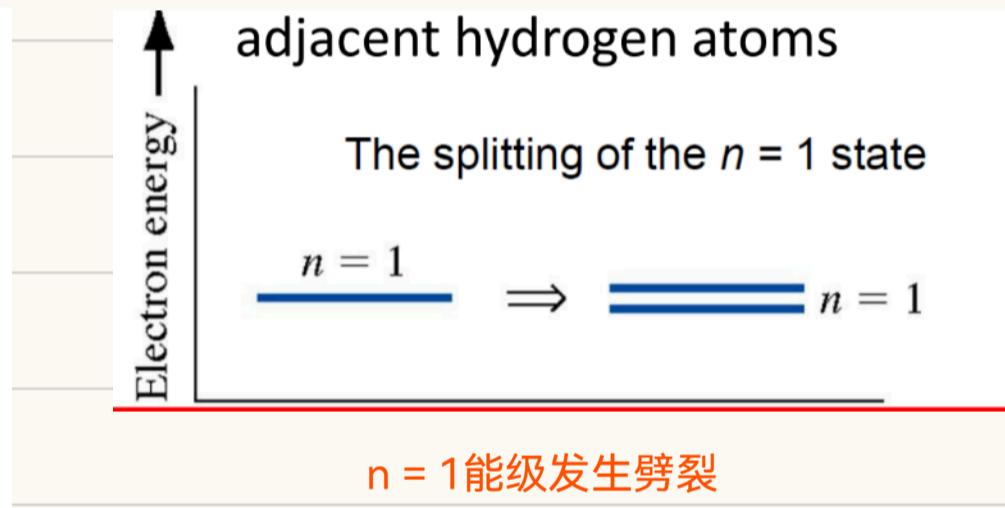
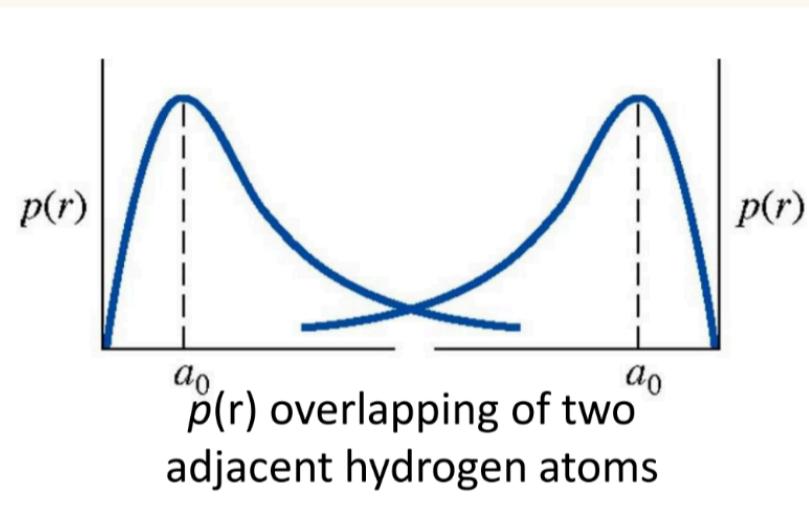
能带模型

有关电子位置的PDF

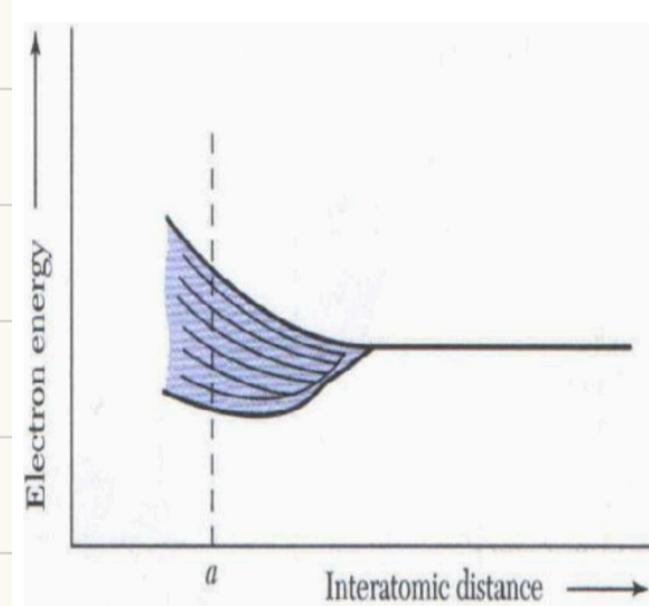
一个氢原子时



两个氢原子从远处靠近时

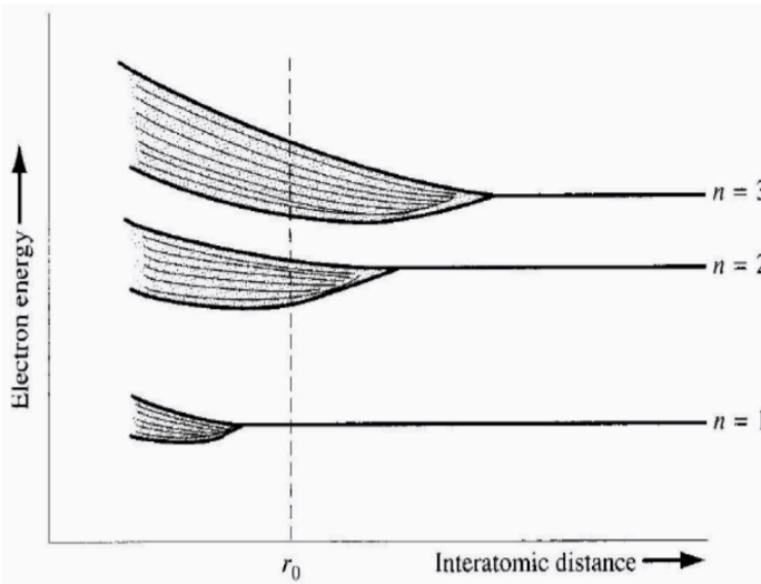


N个氢原子从远处靠近



能级劈裂成准连续的结构，逐渐形成能带

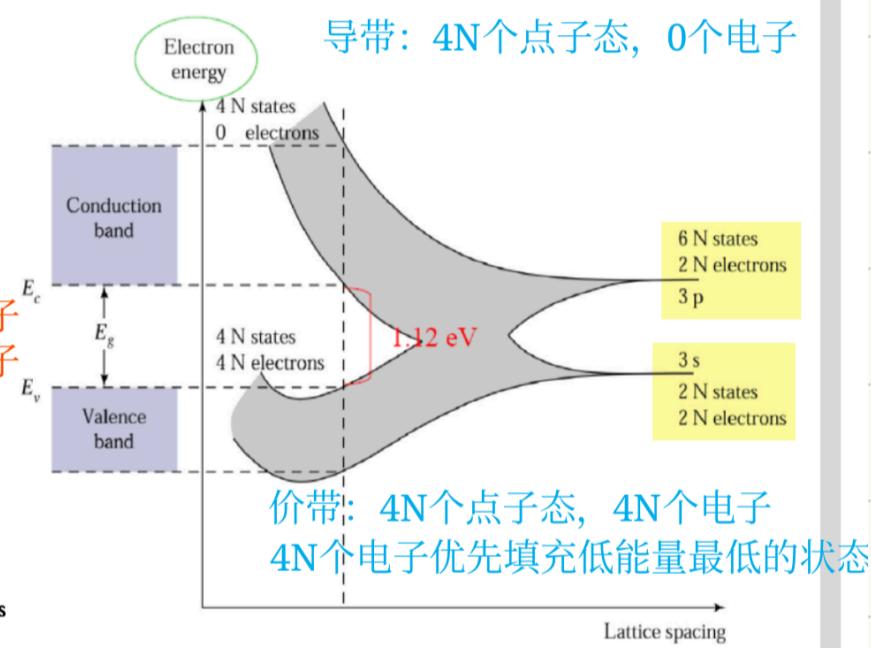
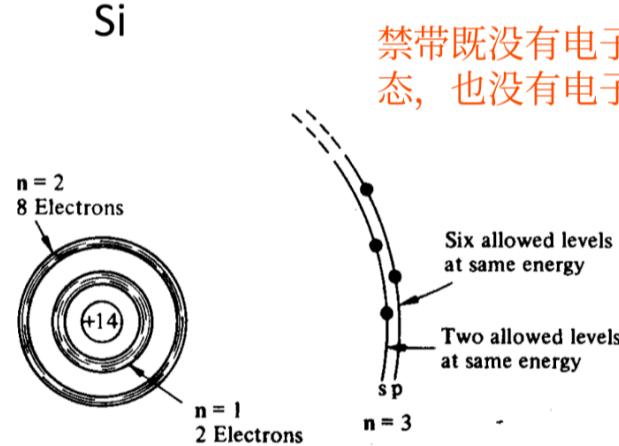
多电子原子



对于具有多个电子的N原子，随着它们之间的距离减小，它们在不同状态下的初始量子化能级将逐渐分裂成带。

硅原子

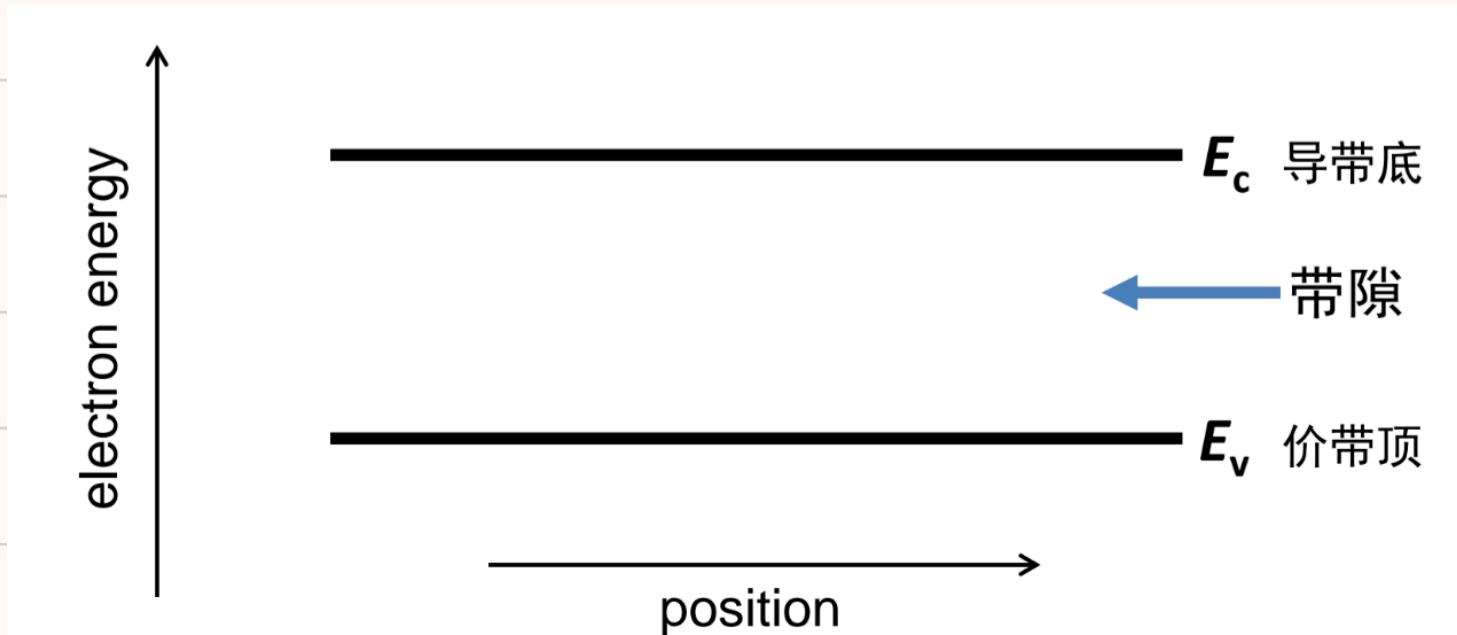
- The energy level of isolated Si atom is $1S^2 2S^2P^6 3S^2P^2$
- Energy band formation of Solid Si



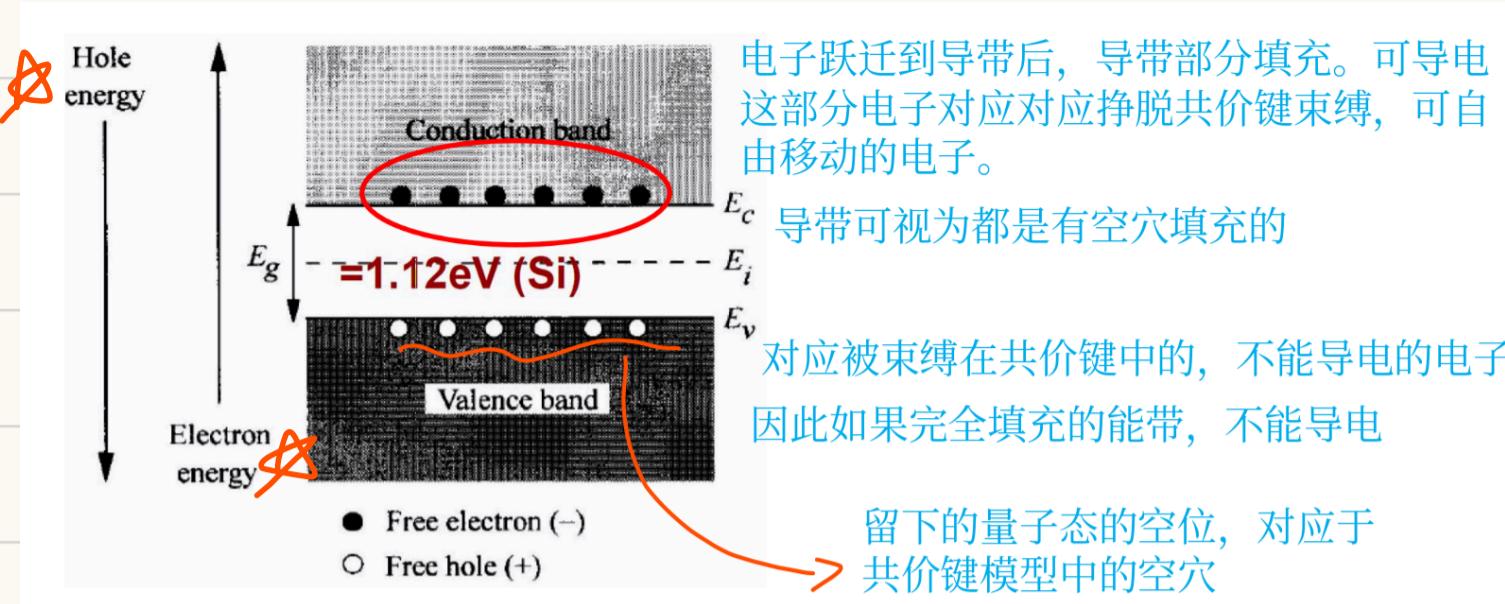
能带图

时空间

简化



能带模型与共价键模型的对应



价带中的电子——被束缚在共价键中的电子

跃迁到导带中的电子——挣脱共价键束缚的电子

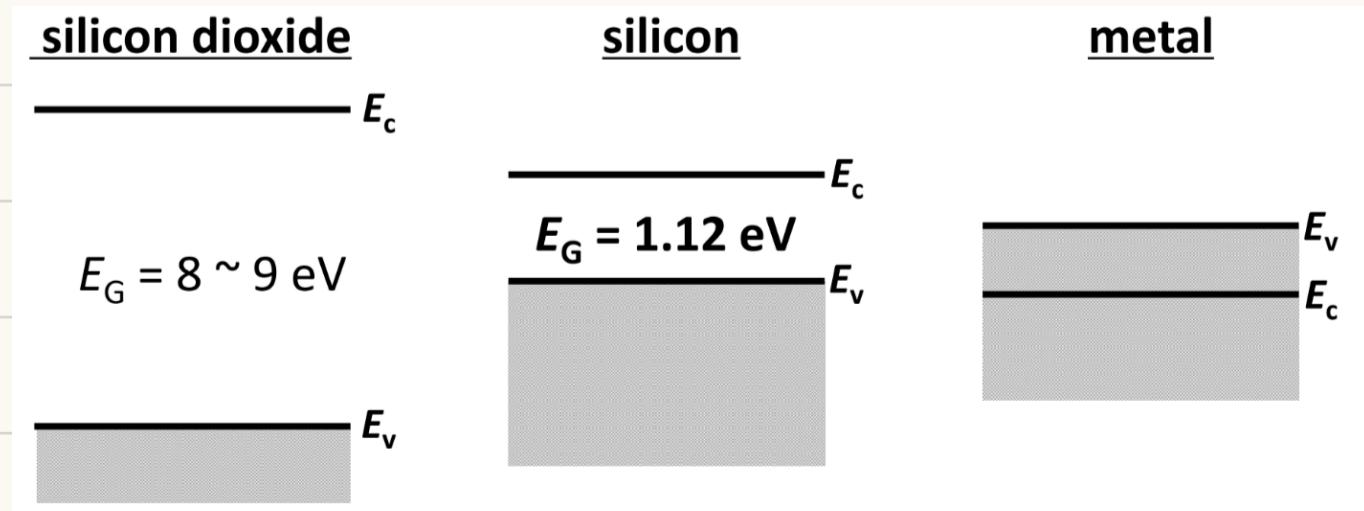
跃迁后价带中遗留的空穴——空穴

Electrons & holes tend to seek lowest-energy positions, Electrons tend to fall and holes tend to float up (like bubbles in water)

Ec可视为电子的势能，对应刚刚好跃迁到导带中，挣脱共价键束缚，成为能导电的电子的势能

E_c represents the electron potential energy. $P.E. = E_c - E_{\text{reference}}$

绝缘体、半导体与金属的能带图



QA：能带模型

DeepSeek R1

什么是能级？

能级是电子所处的能量状态，不同能级对应不同的能量

关键点：

1. 不同台阶=不同能量：高台阶的电子能量高（像高处的水），低台阶能量低。
2. 跳台阶要能量：电子吃能量（如吸收光）会跳上高层，吐能量（发光）时跳下来。
3. 指纹效应：不同材料的能级差不同，发光颜色就不同（比如霓虹灯发红光，钠灯发黄光）。

比如硅原子，每个核外电子都有自己的能级吗？

单个硅原子的核外电子确实有分立的能级，但固体中的硅（比如晶体硅）会形成能带，而不是孤立的原子能级

对于孤立硅原子：

单个硅原子有14个电子，分布在K/L/M壳层（能级1s, 2s, 2p, 3s, 3p）。

电子按泡利不相容原理和能量最低原理填充能级（比如3p能级有6个电子）。

此时能级是分立的，就像楼梯的台阶（电子只能存在于特定能级）。

.....

很好，现在总结一下，以硅原子为例，总结能级形成能带的结构。要包含以上对我的提问中我的疑点的解答。

第一步：孤立原子的分立能级

想象一个孤立的硅原子，它的电子分布在不同的能级（1s, 2s, 2p, 3s, 3p等），就像楼梯的台阶（下图左）。

- 分立性：电子只能站在某个台阶上，不能站在两级之间（量子化）。
- 能量差固定：比如3s和3p能级之间的能量差是固定的（类似台阶高度固定）。

外层电子(3s, 3p)参与形成能带

内层电子（如1s、2s、2p）的电子云局域在原子核附近，几乎不参与能带形成，能级保持分立。

2. 能级分裂与能带形成

(1) 原子聚集与杂化

- **sp³杂化**: 当硅原子形成晶体时, 3s和3p轨道杂化为4个等价的sp³轨道 (能量介于原3s和3p之间)。
- **成键态与反键态**:
 - **成键态**: 相邻原子的sp³轨道同相位叠加, 能量降低, 形成共价键。
 - **反键态**: 相邻原子的sp³轨道反相位叠加, 能量升高。

(2) 能带形成

- **价带**: 所有原子的成键态能级密集分裂, 形成**连续能带** (被电子填满)。
- **导带**: 所有原子的反键态能级密集分裂, 形成**连续能带** (未填充电子)。
- **带隙**: 价带顶部与导带底部之间的能量禁区 (硅约1.1 eV)。

关键疑问解答

为什么3s能级会分裂成N个能级?

- **量子力学根源**: 当N个原子靠近时, 每个原子的3s电子会感受到**其他原子的势场** (核电荷+电子云)。
- **波函数重叠**: 根据量子力学, 电子波函数重叠会导致**简并解除** (原本相同的能级因环境不同而分裂)。
- **泡利不相容原理**: 每个能级最多容纳2个电子 (自旋相反)。N个原子的3s轨道必须提供N×2个电子位置, 因此分裂为N个能级。

类比: 想象N个相同音叉, 若彼此靠近, 振动会相互干扰, 导致频率略微不同 (类似能级分裂)。



3s能级分裂成的N个能级能量是否相同?

- **能量不再相同**: 分裂后的能级能量会分布在原3s能级附近的一个范围内, 形成能带。
- **能带宽度**: 能量范围由原子间距和相互作用强度决定。例如, 硅的3s能带宽度约几电子伏特 (eV)。

分裂后的能级会高于3p或低于2p吗?

- **能量相对关系**:
 - **3s能带**: 分裂后的能量范围仍**低于3p能带** (因为孤立原子中3s能级本就低于3p)。
 - **与2p能级的关系**: 2p是内层能级, 几乎不受原子聚集影响, 保持分立且能量远低于3s能带。

示意图：

保存 复制

- 1 孤立原子能级： 2p (分立)
- 2 3s (分立) → 劈裂为3s能带 (能量范围接近原3s)
- 3 3p (分立) → 劈裂为3p能带 (能量范围接近原3p)

- 杂化效应：在硅晶体中，3s和3p能带会进一步杂化形成sp³杂化能带，再分裂为价带和导带。

sp³杂化轨道是能级吗？如果是，其能量状态是怎样的？

- 是的，但需注意：sp³杂化是原子轨道的线性组合，形成新的杂化轨道（能量介于原3s和3p之间）。
- 杂化后的能量：单个sp³杂化轨道的能量高于原3s，但低于原3p（具体数值因原子类型和成键环境而异）。

$$1s < 2s < 2p < 3s < sp^3 < 3p$$

导带和价带的能量相比sp³, 2s, 2p, 3p的能量大小是怎样的？

在硅晶体中：

- 价带：由sp³杂化轨道的成键态演化而来，能量低于原sp³杂化轨道。
- 导带：由sp³杂化轨道的反键态演化而来，能量高于原sp³杂化轨道。
- 带隙：价带顶部与导带底部之间的能量差（硅约1.1 eV）。

$$1s < 2s < 2p < \text{价带} < sp^3 < \text{导带} < 3p$$

还有一点不懂。就是你说的“导带：由未填充电子的高能级（如3p）劈裂形成，对应晶体中的反键态。”3p轨道不是已经和3s轨道杂化形成sp³轨道了吗？为什么你说它未填充电子？导带到底是怎么形成的呢亲？

关键修正与补充

1. 导带并非直接由孤立原子的3p轨道形成，而是由sp³杂化后的反键态演化而来。
2. 杂化与能带分裂是导带和价带形成的核心步骤。

这里有一个重点，在绝对零度时，外层电子全部在价带，导带无电子。（这是对于半导体，如果是导体，绝对零度下导带有可能填充有部分电子）

为什么未激发时导带是空的？

- 电子填充规则：在形成晶体时，所有成键态（价带）已被电子占满（硅有4个价电子，正好填满4个成键态）。
- 反键态（导带）能量较高，在未受热或光照时，电子无法跃迁到导带，因此导带初始为空。

简洁点来说

成键态已填满：硅有4个价电子，正好填满4个成键态（价带）。

反键态能量高：导带对应反键态，需外界能量（如热、光）激发电子跃迁至此。

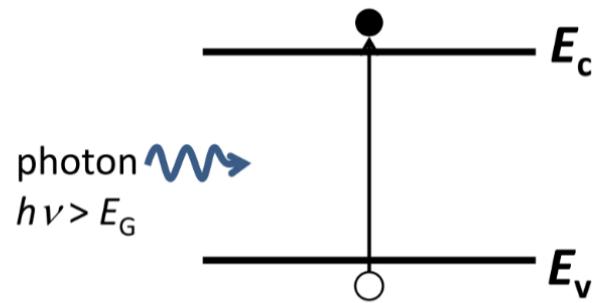
导带和价带的能量为何不连续？

回归薛定谔方程！

- 成键与反键的本质差异：成键态（价带）能量低，反键态（导带）能量高，两者之间天然存在带隙。
- 量子力学禁带：周期性势场下，薛定谔方程的解在能量空间中存在禁区（带隙）。

EG的测定

E_G can be determined from the minimum energy of photons that are absorbed by the semiconductor



Band gap energies of selected semiconductors

Semiconductor	Ge	Si	GaAs
Band gap energy (eV)	0.67	1.12	1.42

动量空间中的能带模型

E-k Relationship for Free Electron

- De Broglie Equation:

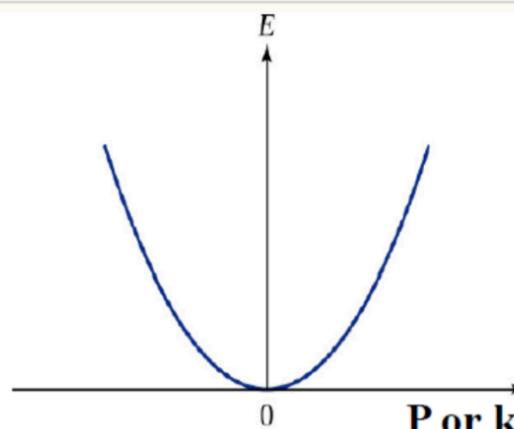
$$p = \hbar k$$

- Solution of Schrödinger Equation for free space electron:

$$\Psi(x, t) = A \exp[j(kx - \omega t)] + B \exp[-j(kx + \omega t)]$$

$$\text{where } k = \sqrt{\frac{2m_0 E}{\hbar^2}}$$

$$\Rightarrow E = \frac{\hbar^2 k^2}{2m_0}$$

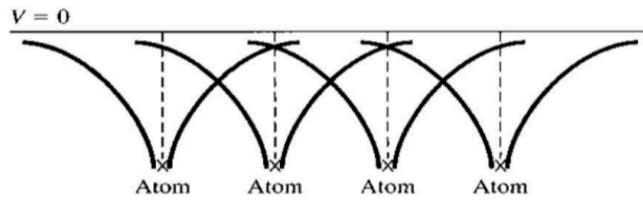


The parabolic E-k relation
for free space electron
自由空间电子的抛物E-k关系

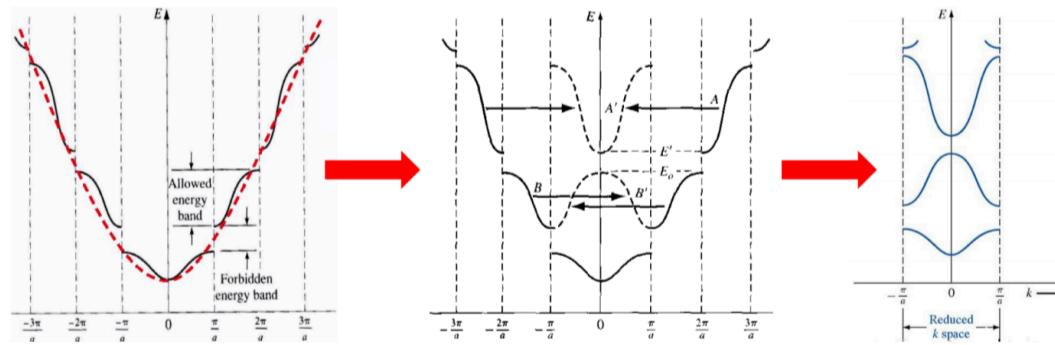
E-k diagram describes the relationship
between the energy and the momentum in
the momentum space! 动量空间

The k-Space Diagram in a Single Crystal

- Periodic potential of a 1D lattice:



- Periodic potential \rightarrow discontinuity of energy at $k = n\pi/a \rightarrow$ Band gap:



E-k图：

① E-k关系不连续，体现了能量的不连续性。

连续的部分称为**允带**：即**价带**和**导带**，间断的部分称为**禁带**。

② a 为晶格常数。在实空间中， a 为周期(因为无限范围内，平移 a 后晶格不变)。
因此在**动量空间**中， $2\pi/a$ 是周期。

因此E-k图平移 $2\pi/a$ 的整数倍是合理的。

基于E-k diagram对半导体分类

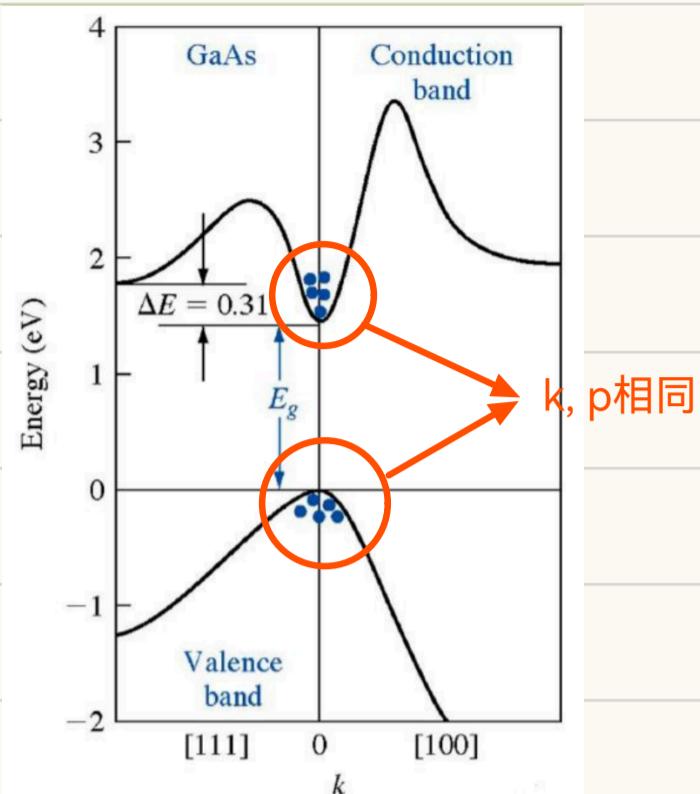
Direct Gap Semiconductor

例如: GaAs, InP, GaN, ZnO

The top of the highest (occupied) valence band and the bottom of the lowest (unoccupied) conduction band are at the same value in k-space.

最高价带的价带顶与最低导带的导带底有相同动量。

特点



光物质相互作用容易发生，价带顶电子吸收入射光子的能量容易跃迁到导带底。

为什么容易发生?

因为很容易满足:

- ① 动量守恒(k同, p同, 动量远大于光子动量, 光子动量可忽略不计)
- ② 能量守恒(对应频率即可)

因此: The generation efficiency of photoelectron is high \rightarrow Application in semiconductor laser and other luminous devices

光电子的产生效率高，在半导体激光器和其他发光器件中的应用

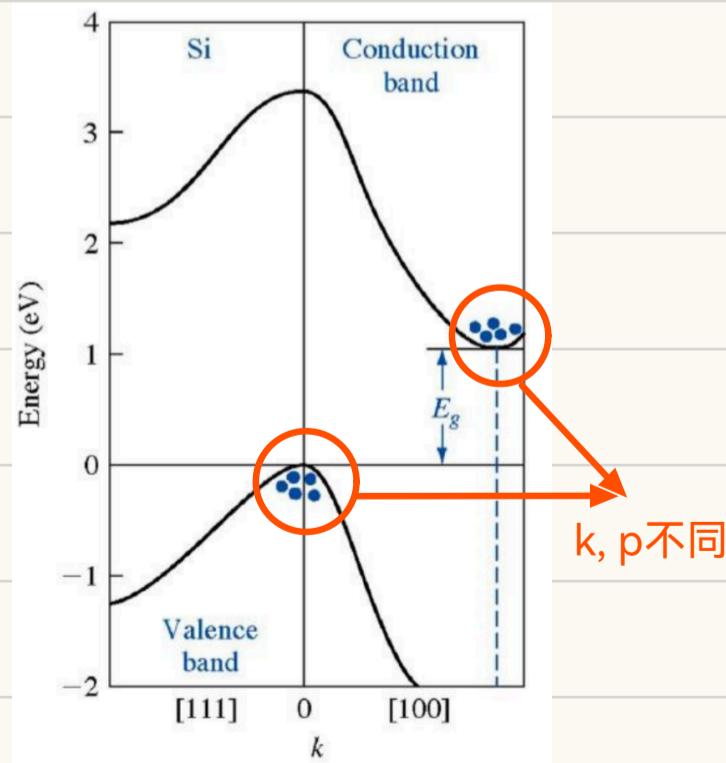
Indirect Gap Semiconductor 间接带隙半导体

例如: Ge, Si, GaP, AlAs

The top of the highest (occupied) valence band and the bottom of the lowest (unoccupied) conduction band are at different k-values.

最高价带的价带顶与最低导带的导带底有不同动量。

The momentum mismatch via the electron transition from valence band to conduction band has to be compensated.



通过电子从价带跃迁到导带的动量失配必须得到补偿。

为了满足动量守恒: $\hbar k' - \hbar k = \hbar k_{\text{photon}} \pm \hbar q$

- Interaction with the lattice is needed.
- The momentum mismatch is compensated by the phonon(声子) emission/absorption.
声子既有能量也有动量，通过声子的吸收和释放，补偿跃迁过程中的动量差。因此间接带隙半导体光电子跃迁的难度要大于直接带隙半导体。

QA: 能带模型 DeepSeek R1

1. 为什么k会有负值？

- **k的本质**: k是电子的晶格动量（或波矢），描述电子波在晶体中的传播方向。
- **正负的意义**: k的正负代表波的传播方向相反。例如：
 - $k=+\pi/a$ 表示波向右传播。
 - $k=-\pi/a$ 表示波向左传播。
- **周期性边界**: 在晶格中，k被限制在第一布里渊区（如 $-\pi/a \leq k \leq \pi/a$ ），负k是方向相反的合法状态。

2. 为什么存在多个导带和价带？

(1) 原子轨道的多样性

- 孤立原子有多个能级（如3s、3p、3d等），当原子形成晶体时，**每个原子轨道都会劈裂成能带**。
- 例如：硅的3s和3p轨道杂化形成sp³能带，但更高能级的轨道（如3d）也可能参与形成其他能带。

(2) 晶格对称性

- 不同方向的动量(k)对应不同的电子运动模式，导致能带在动量空间中呈现多分支。
- 例如：在硅的布里渊区中，沿Γ-X、Γ-L等方向的能带形状不同，形成多个极值点。

(3) 自旋轨道耦合

- 电子的自旋与轨道运动相互作用，可能↓使能带进一步分裂（如重金属中的强自旋轨道耦合效应）。

3. 多导带和价带的实例

(1) 硅的能带结构

- **价带**: 由sp³杂化轨道的成键态形成，包含多个子带（如重空穴带、轻空穴带、自旋轨道分裂带）。
- **导带**: 由反键态形成，包含多个极小值（如Δ轴、L点附近的导带底）。

(2) 金属（如铜）

- 多个能带部分填充，无明确带隙，所有能带均可参与导电。

4. 如何从E-k图中识别导带和价带？

1. **能量高低**: 低能区为价带，高能区为导带。
2. **电子占据**: 费米能级 (E_F) 的位置:
 - **半导体/绝缘体**: 费米能级位于价带顶和导带底之间。
 - **金属**: 费米能级穿过能带。
3. **带隙判断**: 若两个能带之间无电子态（能量禁区），则低能带为价带，高能带为导带。

有效质量

Concept

In solid state physics, the electron's effective mass (m^*) is the mass that it seems to have when responding to forces, or when interacting with other particles.

Why effective mass

The movement of particles in a periodic potential can be very different from their motion in a vacuum (like a glass marble in a container with water or oil). The effective mass is a quantity that is used to simplify band structures by modeling the behavior of a free particle with that mass.

核心问题: 真空中电子运动遵循牛顿定律 ($(F = m_0 a)$)，但在晶体中，电子受周期性势场影响，运动规律复杂。

有效质量的本质: 将晶格势场对电子的作用等效为质量的变化，使牛顿定律形式得以保留 ($(F = m^* a)$)。

实际意义:

- 简化载流子动力学分析（如半导体器件中的电子输运）。
- 直接关联能带曲率，反映电子对外场的响应速度。

Value of m^*/m_e

Usually in the range 0.01 to 10, but can be lower or higher, can vary depending on a number of factors.

Determination of m^*

- For a free electron (or classical particle):

$$E = \frac{P^2}{2m_e} \Rightarrow m_e = \left[\frac{d^2 E}{dP^2} \right]^{-1}$$

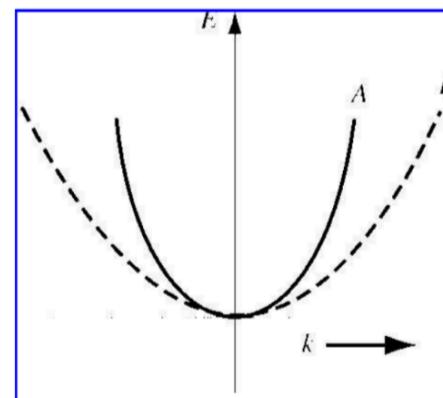
- m^* is determined from the E-k relation:

有效质量正相关于曲率倒数，即曲率半径

$$m^* = \left[\frac{d^2 E}{dP^2} \right]^{-1} = \left[\frac{d^2 E}{\hbar^2 dk^2} \right]^{-1} = \hbar^2 \left[\frac{d^2 E}{dk^2} \right]^{-1}$$

- If an electric field is applied on the electron, the acceleration is:

$$a = \frac{-eE}{m^*}$$



For electrons at the bottom of the conduction band:
Larger curvature \rightarrow smaller effective mass, so $m_B^* > m_A^*$

有效质量正相关于曲率倒数，即曲率半径

电子/空穴的有效质量与能带的关系

原始方程: $\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2}$

➤ Electron at the conduction band bottom:

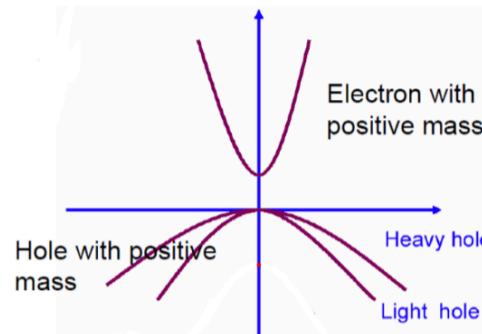
- $E''(k) > 0 \rightarrow m_n^* > 0$

➤ Valence band top:

- For electron: $E''(k) < 0 \rightarrow m_n^* < 0$ (like an ice cube moving upward in the water)
- The electron with negative m_n^* is similar to a hole with positive m_p^*

$$F = m_n^* a = -eE$$

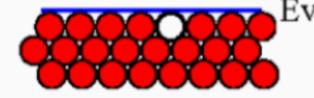
$$a = \frac{-eE}{-|m_n^*|} = \frac{+eE}{|m_n^*|} = \frac{+eE}{m_p^*}$$



Electron free to move in conduction band



Ev



“Hole” free to move in valence band

电子(n) 导带底的电子有效质量为正，价带顶的电子有效质量为负。

同样力的作用下，空穴的运动状态与电子相反，因此：

空穴(p) 导带底的空穴有效质量为负 价带顶的空穴有效质量为正。

导带底的电子的有效质量不等于价带顶的空穴的有效质量，因为导带和价带的形状不一定相同而且大概率不同

300K时的有效质量

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

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

一般考虑价带顶的空穴和导带底的电子，即本征载流子

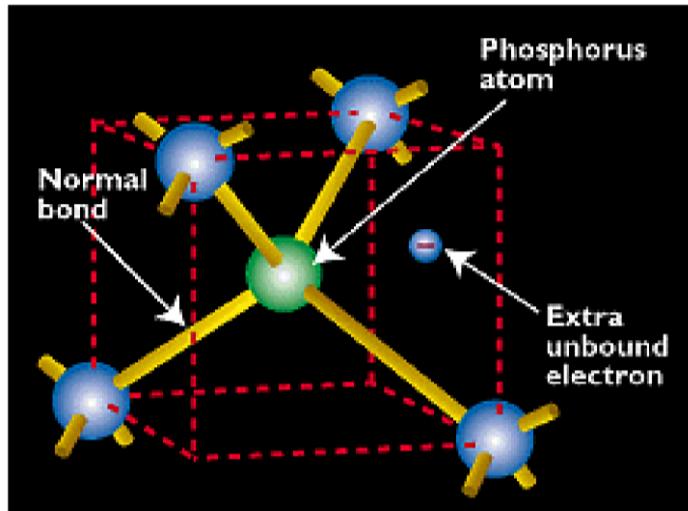
掺杂

Doping — Carrier Concentration Control

载流子浓度控制

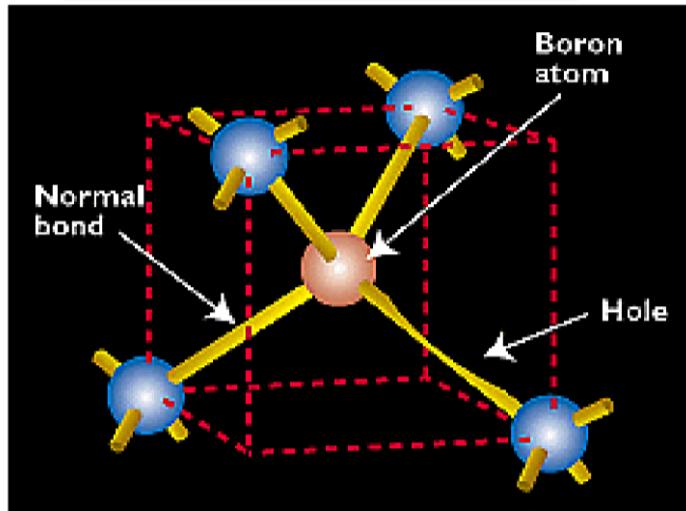
- By substituting a Si atom with a special impurity atom (Column V or Column III element), a conduction electron or hole is created.

Donors: P, As, Sb 施主



$N_D \equiv$ ionized donor concentration (cm^{-3})

Acceptors: B, Al, Ga, In 受主



$N_A \equiv$ ionized acceptor concentration (cm^{-3})

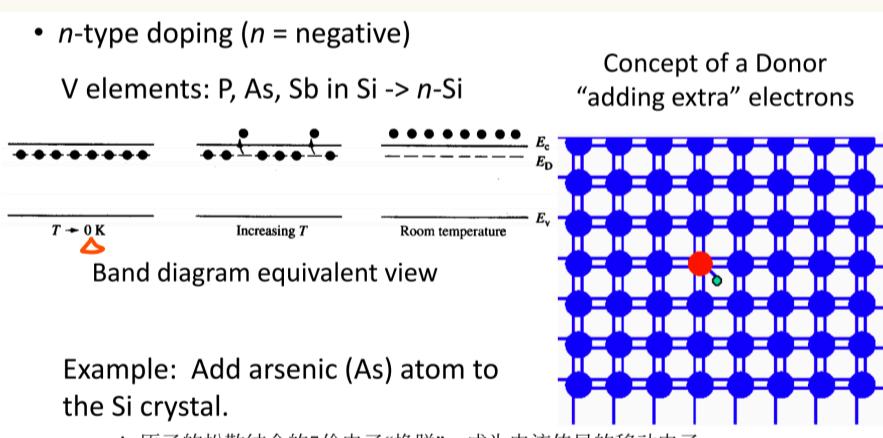
掺杂原子电离浓度

施主与受主的能带

在室温下，可认为所有掺杂原子都被电离

• n-type doping ($n = \text{negative}$)

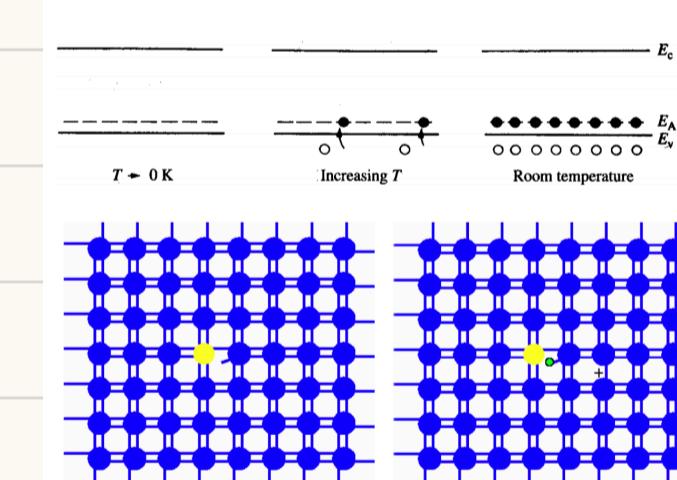
V elements: P, As, Sb in Si \rightarrow n-Si



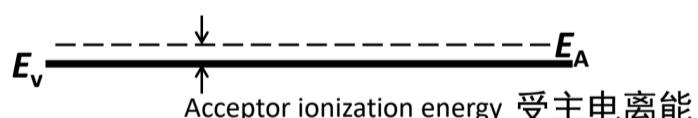
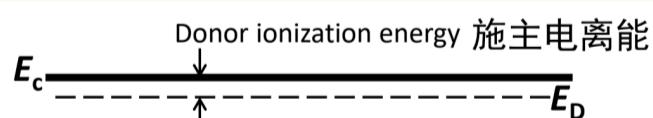
Example: Add arsenic (As) atom to the Si crystal.

As原子的松散结合的5价电子“挣脱”，成为电流传导的移动电子。
The loosely bound 5th valence electron of the As atom “breaks free” and becomes a mobile electron for current conduction.

• p-type doping ($p = \text{positive}$): III elements: B, Al, Ga, In in Si \rightarrow p-Si



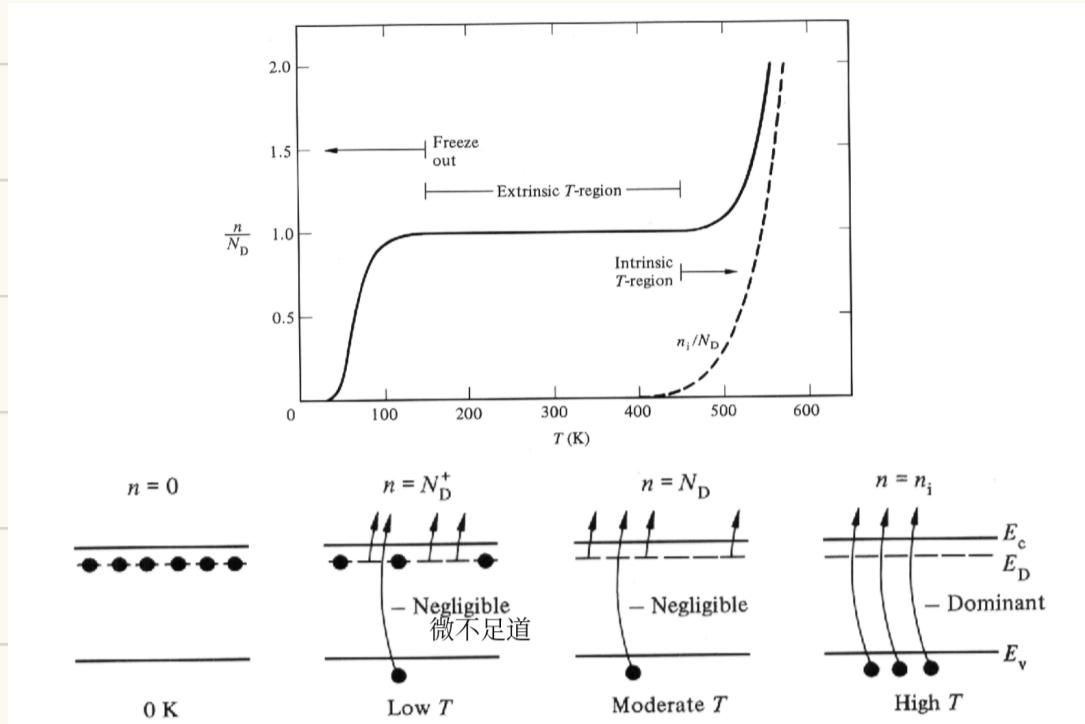
The III atom accepts an electron from a neighboring Si atom, leaving a “hole” there. The hole is free to hop around the silicon lattice, carrying current with positive charges.



硅中特定施主和受主的电离能
Ionization energy of selected donors and acceptors in silicon

Dopant	Donors			Acceptors		
	Sb	P	As	B	Al	In
Ionization energy (meV) $E_c - E_D$ or $E_A - E_v$	39	45	54	45	67	160

Carrier Concentration vs. Temperature in Doped Semiconductor



Carrier Concentration at Thermal Equilibrium

热平衡态下的载流子浓度

Thermal Equilibrium 热平衡状态

- No external forces are applied:
 - electric field = 0, magnetic field = 0
 - mechanical stress = 0
 - no light
- Dynamic situation in which every process is balanced by its inverse process 每个过程都由其逆过程平衡的动态情况
 - Electron-hole pair (EHP) generation rate = EHP recombination rate 重组
热骚动
- Thermal agitation → electrons and holes exchange energy with the crystal lattice and each other
 - Every energy state in the conduction band and valence band has a certain probability of being occupied by an electron
导带和价带中的每个能态都有一定的概率被电子占据

常数

- Electronic charge, $q = 1.6 \times 10^{-19} \text{ C}$ 元电荷
- Permittivity of free space, $\epsilon_0 = 8.854 \times 10^{-14} \text{ F/cm}$ 真空介电系数
- Boltzmann constant, $k = 8.62 \times 10^{-5} \text{ eV/K}$ 玻尔兹曼常量
- Planck constant, $h = 4.14 \times 10^{-15} \text{ eV}\cdot\text{s}$ 普朗克常量
- Free electron mass, $m_e = 9.1 \times 10^{-31} \text{ kg}$ 自由电子质量
- Thermal voltage $kT/q = 26 \text{ mV}$ at room temperature
- $kT = 0.026 \text{ eV} = 26 \text{ meV}$ at room temperature
- $kT/\ln(10) = 60 \text{ meV}$ at room temperature

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ Joules}$$

Density of States 态密度 $g(E)$



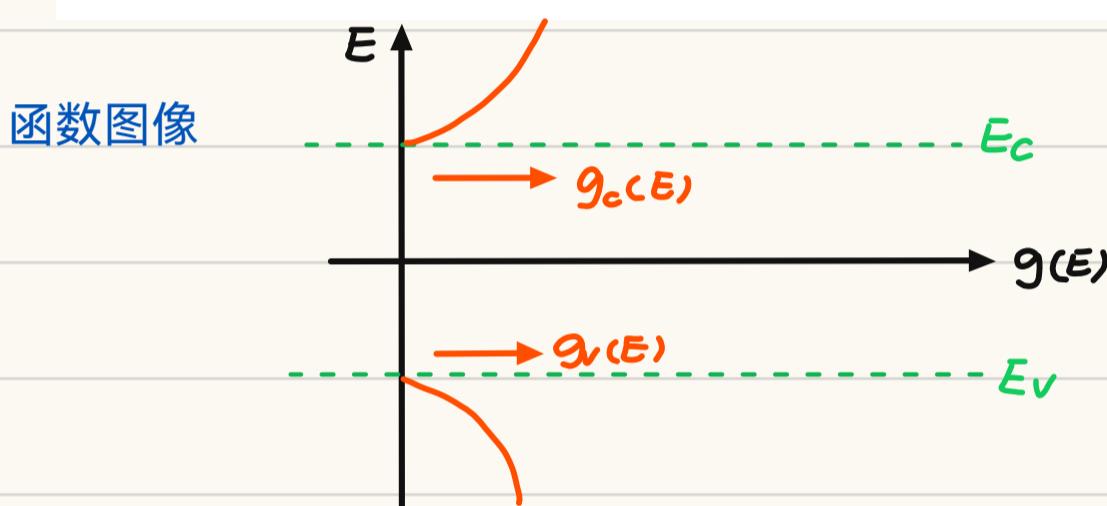
$g(E)dE = \text{number of states per cm}^3 \text{ in the energy range between } E \text{ and } E+dE$ E和E+dE之间能量范围内每立方厘米的态数
态数：即量子态数，不是电子数，而是最多占据的电子数

Near the band edges:

$$g_c(E) = \frac{8\pi\sqrt{2}}{h^3} (m_n^*)^{3/2} \sqrt{(E - E_c)} \quad \text{for } E \geq E_c$$

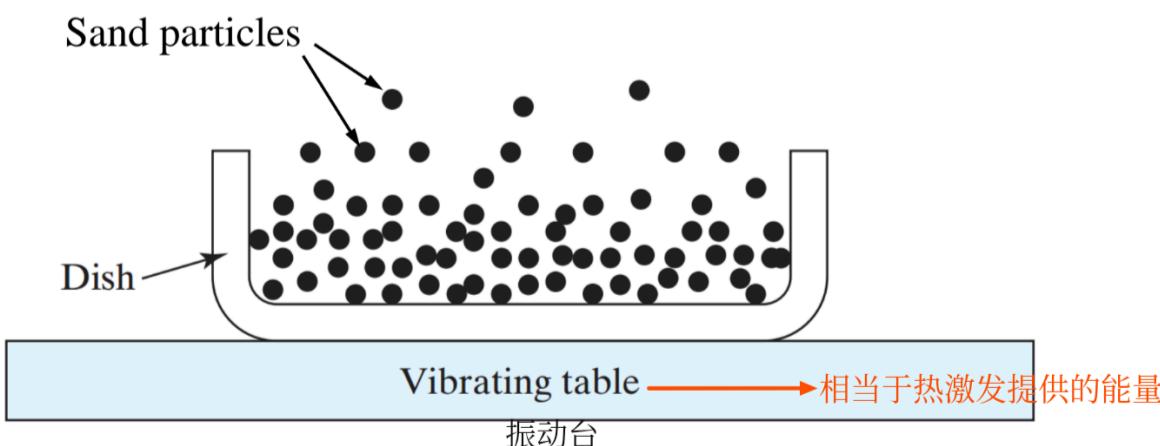
$$g_v(E) = \frac{8\pi\sqrt{2}}{h^3} (m_p^*)^{3/2} \sqrt{(E_v - E)} \quad \text{for } E \leq E_v$$

unit: $\left(\frac{\text{Number of States}}{\text{cm}^3} \right) / \text{eV}$



理解：类比

Analogy for Thermal Equilibrium



- There is a certain probability for the electrons in the conduction band to occupy high-energy states under the agitation of thermal energy (vibrating atoms).

Fermi Distribution Function 费米分布函数

能量E处的可用状态被电子占用的概率，更准确的来说，是比率

- Probability that an available state at energy E is occupied:

$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}$$

- E_F is called the **Fermi energy** or the **Fermi level**. 费米能级
- k is the Boltzmann Constant and T is the temperature (K). 玻尔兹曼常量
- $1 - f(E)$ is the probability that a state at energy E is unoccupied. 被空穴占用的比率

There is only one Fermi level in a system at equilibrium.

在热平衡状态下，只有一个费米能级

If $E \gg E_F$: $f(E)$ approaches 0

If $E \ll E_F$: $f(E)$ approaches 1

If $E = E_F$: $f(E) = 1/2$

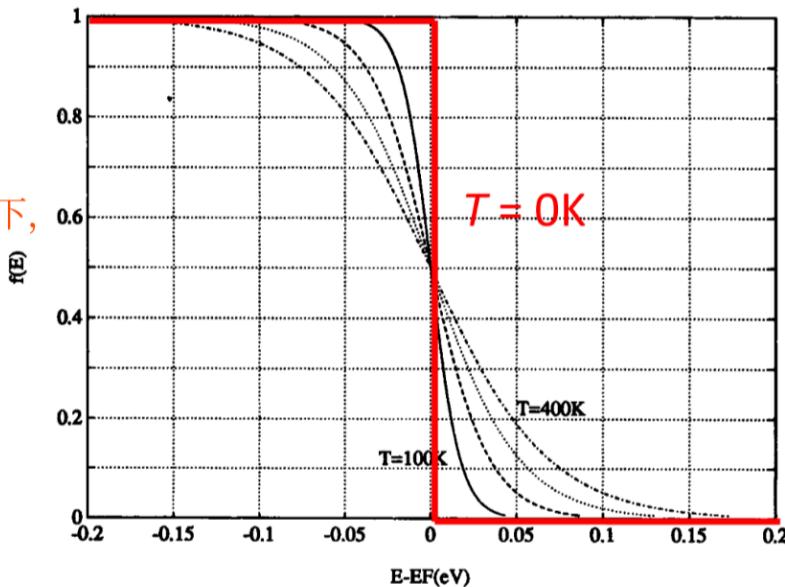
$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}$$

费米能级是绝对零度下，
电子占据的最高能级

If $T = 0$, $E > E_F$: $f(E) = 0$

$E < E_F$: $f(E) = 1$

No occupation of states above E_F and complete occupation of states below E_F .

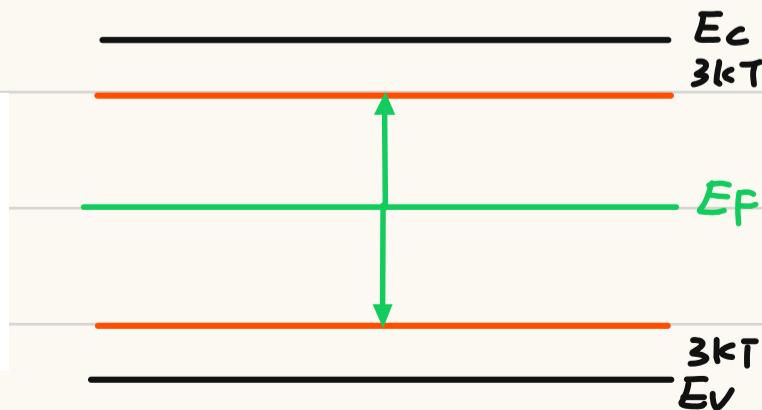


费米分布函数与玻耳兹曼近似

Boltzmann Approximation

轻掺杂时：

- $E \gg E_F$ i.e. $E-E_F > 3kT$: $f(E) \approx e^{-(E-E_F)/kT}$
- $E \ll E_F$ i.e. $E_F-E > 3kT$: $1 - f(E) \approx e^{-(E_F-E)/kT}$
- $E = E_F$: $f(E) = 1/2$



$$\textcircled{1} \quad f(E) = \frac{1}{1 + e^{(E-E_F)/kT}} = \frac{e^{-(E-E_F)/kT}}{1 + e^{-(E-E_F)/kT}}$$

$\frac{1}{1+x} \approx 1 - x$ for $x \gg 1$
 $E - E_F > 3kT$

$$= e^{-(E-E_F)/kT} (1 - e^{-(E-E_F)/kT})$$

$$\approx e^{-(E-E_F)/kT}$$

$$\textcircled{2} \quad f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}$$

$$\rightarrow 1 - f(E) = \frac{e^{(E-E_F)/kT}}{1 + e^{(E-E_F)/kT}}$$

$\frac{1}{1+x} \approx 1 - x$ for $x \gg 1$
 $E_F - E > 3kT$

$$= e^{(E-E_F)/kT} (1 - e^{(E-E_F)/kT})$$

$$\approx e^{(E-E_F)/kT} = e^{-(E_F-E)/kT}$$

物理意义:

Boltzmann approximation:

$$\triangleright E \gg E_F \text{ i.e. } E - E_F > 3kT: f(E) \approx e^{-(E-E_F)/kT}$$

麦克斯韦-玻耳兹曼统计

Maxwell-Boltzmann statistics:

No interaction between particles

$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}$$

轻掺杂，体系中的电子浓度较低，电子之间的距离较远，可以忽略电子之间的相互作用

费米-狄拉克统计

Fermi-Dirac statistics:

Pauli exclusion principle

(Pauli 不相容原理)

Carrier Density in an Energy Interval

能量区间中的载流子密度

导带电子浓度

$$g_c(E)f(E)dE$$

Electrons/cm³ in the

conduction band between
E and E + dE (if E ≥ E_c).

价带空穴浓度

$$g_v(E)(1-f(E))dE$$

Holes/cm³ in the valence

band between E and E +
dE (if E ≤ E_v).

载流子浓度计算

Intrinsic Semiconductor at Thermal Equilibrium

本征半导体

n(E) = g(E)f(E) \quad c = \int n(E)dE

Energy band diagram

Density of States, $g(E)$

\times Probability of occupancy, $f(E)$

= Carrier distribution, $n(E)$

n, p unit: $\text{↑}/\text{cm}^3$

对于本征半导体: $n = p = n_i$

n-Type Semiconductor at Thermal Equilibrium

n型掺杂半导体

n型掺杂，费米能级不再是在禁带中间，而是略微上移。
因为费米能级表示绝对零度时，电子能填充的最高能级。
而n型掺杂天然就有较多的电子，能填充到更高能级。

➤ n -type semiconductor: donor (P, As in Si)

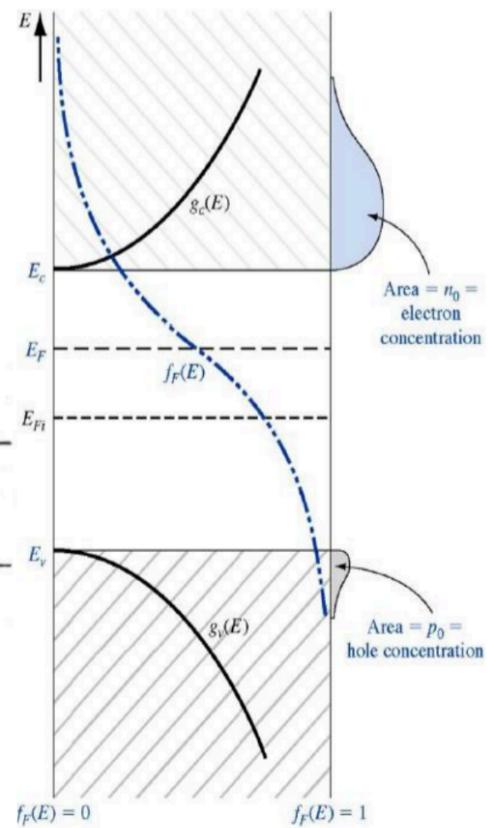
➤ Fermi level moves up to E_c .

Energy band diagram

Density of states

Occupancy factors

Carrier distributions



p-Type Semiconductor at Thermal Equilibrium

情况与n型相反

计算导带电子的密度

$$n = \int_{E_c}^{E_{top}} g_c(E) f(E) dE$$

$$g_c(E) = \frac{8\pi\sqrt{2}}{\hbar^3} (m_n^*)^{\frac{3}{2}} \sqrt{E - E_c} \quad f(E) = \frac{1}{1 + e^{(E - E_F)/kT}}$$

$$\gamma = (E - E_c)/kT \quad \gamma_c = (E_F - E_c)/kT \quad dy = \frac{1}{kT} dE$$

$$n = \int_{E_c}^{E_{top}} \frac{m_n^* \sqrt{2m_n^*(E - E_c)}}{\pi^2 \hbar^3} \frac{1}{1 + e^{(E - E_F)/kT}} dE$$

$$= \frac{m_n^* \sqrt{2m_n^*} (kT)^{\frac{3}{2}}}{\pi^2 \hbar^3} \int_0^\infty \frac{y^{\frac{1}{2}}}{1 + e^{y - \gamma_c}} dy$$

$$= \frac{m_n^* \sqrt{2m_n^*} (kT)^{\frac{3}{2}}}{\pi^2 \hbar^3} F_{1/2}(\gamma_c)$$

$$\gamma_c < -3 (E_F < E_c - 3kT) \text{ 时: } F_{1/2}(\gamma_c) = \frac{\sqrt{\pi}}{2} e^{(E_F - E_c)/kT}$$

$$\rightarrow n = \underbrace{2 \left[\frac{m_n^* kT}{2\pi \hbar^2} \right]^{\frac{3}{2}}}_{N_c} \times \frac{2}{\sqrt{\pi}} F_{1/2}(\gamma_c)$$

$$= \underline{N_c} e^{(E_F - E_c)/kT} \quad N_c = 2 \left(\frac{m_n^* kT}{2\pi \hbar^2} \right)^{\frac{3}{2}} \text{ 导带有效态密度}$$

同理: 价带空穴密度

$$p = \int_{E_{bottom}}^{E_V} g_v(E) (1 - f(E)) dE$$

$$\rightarrow p = N_v e^{(E_V - E_F)/kT} \quad N_v = 2 \left(\frac{m_p^* kT}{2\pi \hbar^2} \right)^{\frac{3}{2}} \text{ 价带有效密度}$$

载流子密度之积——定值

$$np = N_c N_v e^{-E_G/kT} = 4 \sqrt[3]{m_n^* m_p^*} \left(\frac{kT}{2\pi \hbar^2} \right)^3 e^{-\frac{E_G}{kT}}$$

Effective Densities of States at the Band Edges (@ 300K)

	Si	Ge	GaAs
$N_c (\text{cm}^{-3})$	2.8×10^{19}	1.04×10^{19}	4.7×10^{17}
$N_v (\text{cm}^{-3})$	1.04×10^{19}	6.0×10^{18}	7.0×10^{18}

本征半导体的载流子浓度

For an intrinsic semiconductor: $n=p=p_i=n_p, E_F=E_i$

$$n = n_i = N_c e^{-(E_c - E_i)/kT}$$

$$p = p_i = N_v e^{-(E_i - E_v)/kT}$$

$$n_i^2 = N_c N_v e^{-(E_c - E_v)/kT} = N_c N_v e^{-E_G/kT}$$

$$n_i = \sqrt{N_c N_v} e^{-\frac{E_G}{2kT}}$$

The intrinsic carrier concentration depends on T , E_G and m^* .

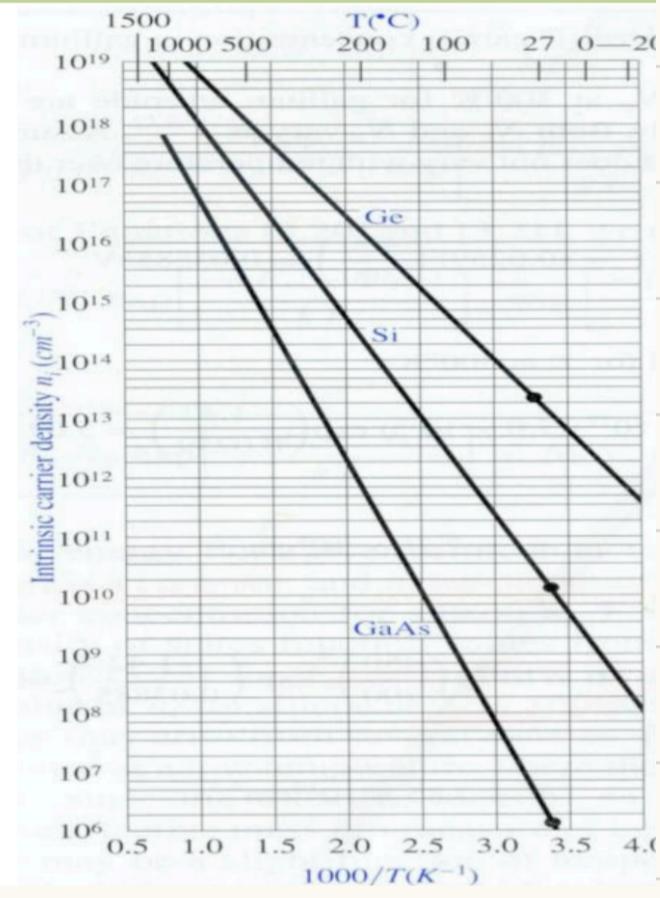
➤ The intrinsic carrier concentration depends on the temperature, the band gap, and the carrier effective mass:

- Higher $T \rightarrow$ Larger n_i
- Larger $E_G \rightarrow$ Smaller n_i

$(E_G: \text{GaAs} > \text{Si} > \text{Ge})$

$$n_i = \sqrt{N_c N_v} e^{-E_G/2kT}$$

$$n_i = 10^{10} \text{ cm}^{-3} \text{ at } 300\text{K for Si}$$



掺杂半导体中的载流子浓度

Charge Neutrality Relationship (电中性关系)

对于均匀掺杂的半导体，正电荷的密度等于负电荷的密度

- For a uniformly doped semiconductor, the density of positive charges is equal to that of negative charges:

$$N_D^+ + p = N_A^- + n$$

电荷守恒定律，正电荷总量等于负电荷总量

N_D^+ : donor number per cm^3 , which has ionized; 电离

N_A^- : acceptor number per cm^3 , which has ionized;

If the donor and acceptor have fully ionized, then:

$$N_D + p = N_A + n$$

N_D : total donor number per cm^3 ;

N_A : total acceptor number per cm^3 .

掺杂半导体载流子浓度计算

- Two assumptions:

- The Boltzmann approximation, i.e. $E_v + 3kT \leq E_F \leq E_c - 3kT$, can be applied (Nondegenerate semiconductor). $\xrightarrow{\text{保证}} np = n_i^2$

- Dopants are fully ionized. (非退化半导体) 轻掺杂半导体、非简并半导体

$$\left. \begin{array}{l} n + N_A = p + N_D \\ np = n_i^2 \Rightarrow p = n_i^2 / n \end{array} \right\} \Rightarrow n^2 + (N_A - N_D)n - n_i^2 = 0$$

$$\Rightarrow n = \frac{N_D - N_A}{2} + \sqrt{\left(\frac{N_D - N_A}{2}\right)^2 + n_i^2}$$

$$\text{Similarly, } p = \frac{N_A - N_D}{2} + \sqrt{\left(\frac{N_A - N_D}{2}\right)^2 + n_i^2}$$

Note: Carrier concentrations depend on net dopant concentration!

检验一个一般式的正确性，应该看能否正确退化为某些特殊情形，如：

几种特殊半导体载流子浓度计算

本征半导体

➤ Intrinsic semiconductor:

$$N_A = N_D = 0 \Rightarrow n = p = n_i$$

$$n = \frac{N_D}{2}$$

n型半导体

➤ N-type semiconductor: n掺杂要求: $N_D > > N_A, N_D > > n_i$

$$N_D - N_A \approx N_D \gg n_i \Rightarrow n = N_D, p = n_i^2 / n$$

$$p = \frac{N_A}{2}$$

p型半导体

➤ P-type semiconductor: 无论掺杂与否, $np=n_i^2$ 为常数

$$N_A - N_D \approx N_A \gg n_i \Rightarrow p = N_A, n = n_i^2 / p$$

高温时

➤ Semiconductor at much high temperature

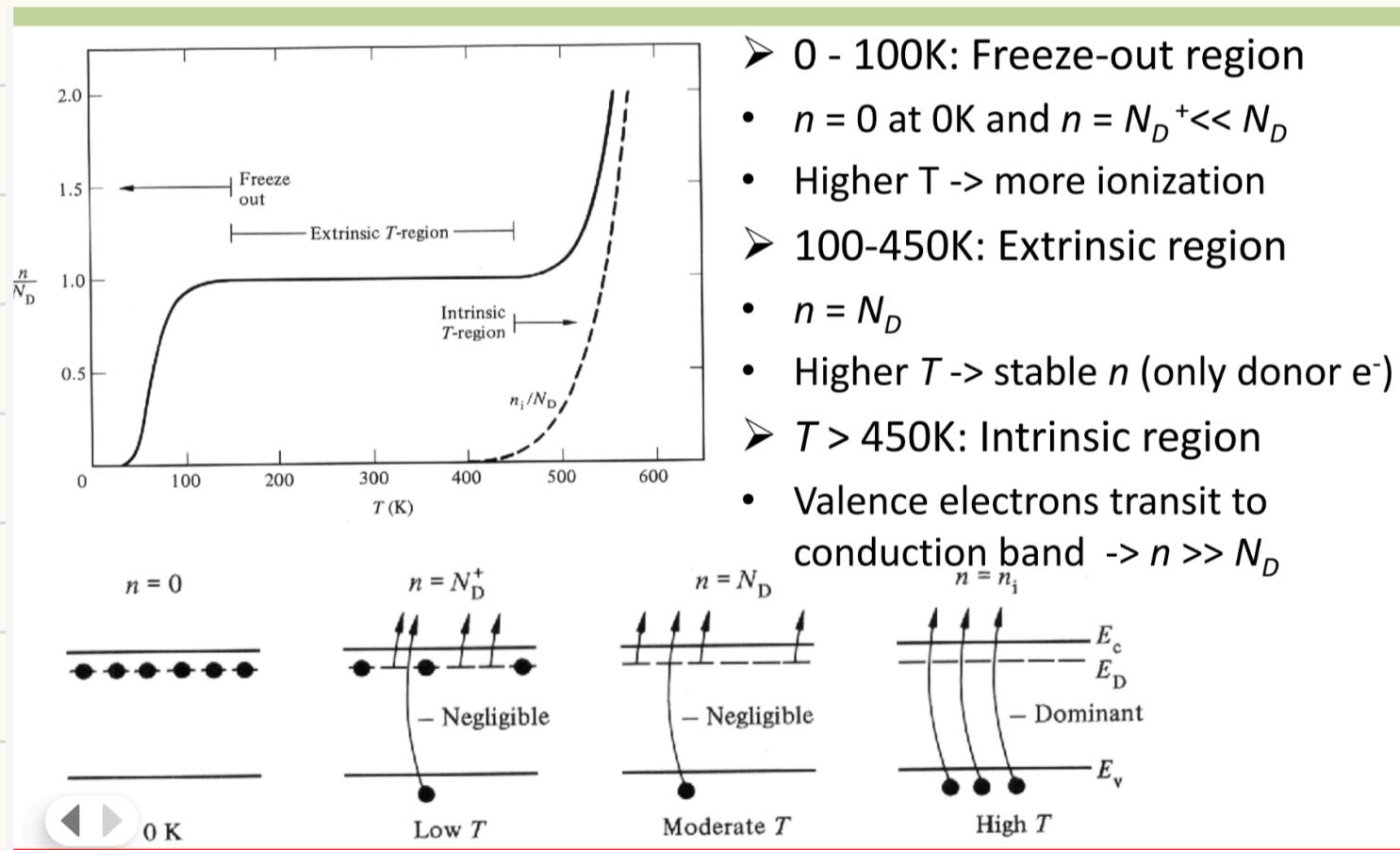
$$n_i \gg |N_D - N_A| \Rightarrow n \approx p \approx n_i \Rightarrow \text{intrinsic semiconductor}$$

补偿半导体

➤ Compensated semiconductor (two types of dopant)

$$N_A \neq N_D \neq 0 \Rightarrow n = \frac{N_D - N_A}{2} + \sqrt{\left(\frac{N_D - N_A}{2}\right)^2 + n_i^2}$$

Revisit the T Dependence of the Carrier Concentration



本征费米能级

$$E_i = \frac{E_c + E_v}{2} + \frac{kT}{2} \ln \frac{N_v}{N_c}$$

- To find E_F for an intrinsic semiconductor, use the fact that $n = p$:

$$N_c e^{-(E_c - E_F)/kT} = N_v e^{-(E_F - E_v)/kT}$$

$$\Rightarrow E_F = \frac{E_c + E_v}{2} + \frac{kT}{2} \ln \left(\frac{N_v}{N_c} \right) \equiv E_i$$

$$E_i = \frac{E_c + E_v}{2} + \frac{3kT}{4} \ln \left(\frac{m_p^*}{m_n^*} \right) \approx \frac{E_c + E_v}{2}$$

- For Si at 300K, the second term is only 0.0073eV, much smaller than the band gap of Si ($E_G = 1.12\text{eV}$).

常见温度范围内，温度对本征费米能级的影响较小

由费米能级、本征费米能级、本征载流子浓度确定载流子浓度

- In an intrinsic semiconductor, $n = p = n_i$ and $E_F = E_i$

$$n = n_i = N_c e^{-(E_c - E_i)/kT}$$

$$\Rightarrow N_c = n_i e^{(E_c - E_i)/kT}$$

$$p = n_i = N_v e^{-(E_i - E_v)/kT}$$

$$\Rightarrow N_v = n_i e^{(E_i - E_v)/kT}$$

- For an extrinsic semiconductor:

$$\begin{aligned} n &= N_c e^{-(E_c - E_F)/kT} \\ &= n_i e^{(E_c - E_i)/kT} e^{-(E_c - E_F)/kT} \end{aligned}$$

$$n = n_i e^{(E_F - E_i)/kT}$$

$$p = N_v e^{-(E_F - E_v)/kT}$$

$$= n_i e^{(E_i - E_v)/kT} e^{-(E_F - E_v)/kT}$$

$$p = n_i e^{(E_i - E_F)/kT}$$

由n, ni以及Ei推导EF

- For nondegenerate (非简并) semiconductor, the Boltzmann approximation, i.e. $E_v + 3kT \leq E_F \leq E_c - 3kT$, can be applied:

$$n = n_i e^{(E_F - E_i)/kT} \quad p = n_i e^{(E_i - E_F)/kT}$$

$$\Rightarrow E_F = E_i + kT \ln\left(\frac{n}{n_i}\right) = E_i - kT \ln\left(\frac{p}{n_i}\right)$$

- When T is high enough or close to 300K, then:

$$E_F = E_i + kT \ln\left(\frac{N_D}{n_i}\right) \quad (N_D \gg N_A, N_D \gg n_i) \quad n\text{-type}$$

$$E_F = E_i - kT \ln\left(\frac{N_A}{n_i}\right) \quad (N_A \gg N_D, N_A \gg n_i) \quad p\text{-type}$$

费米能级与掺杂浓度的关系

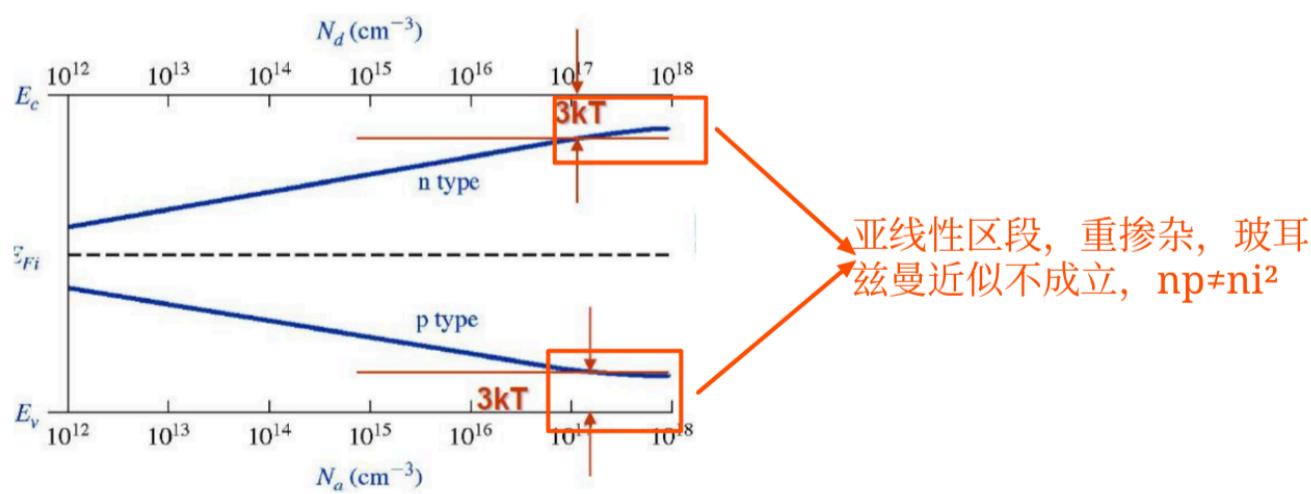
$$E_F = E_i + kT \ln \frac{n}{n_i} \approx E_i + kT \ln \frac{N_D}{n_i}$$

$$= E_i - kT \ln \frac{N_A}{n_i} \approx E_i - kT \ln \frac{N_A}{n_i}$$

- Larger N_A or $N_D \rightarrow E_F$ closer to E_v or E_c

$$E_F = E_i + kT \ln\left(\frac{N_D}{n_i}\right)$$

$$E_F = E_i - kT \ln\left(\frac{N_A}{n_i}\right)$$



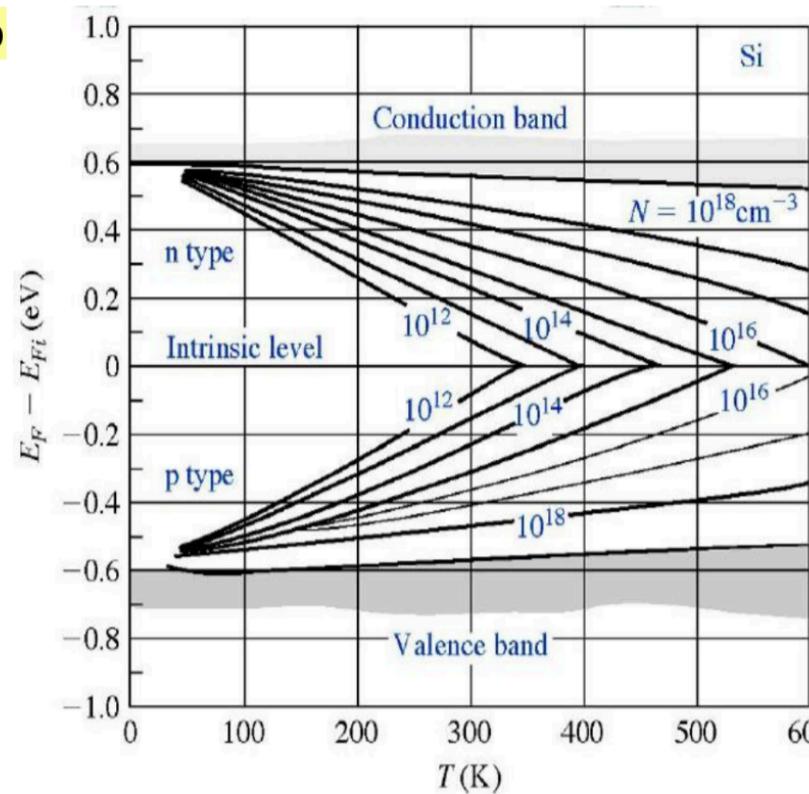
轻掺杂时，掺杂浓度越高，费米能级越接近导带或价带

费米能级与温度的关系

- Larger N_A or $N_D \rightarrow E_F$ closer to E_v or E_c
- Higher T $\rightarrow E_F$ closer to E_i

$$E_F = E_i + kT \ln\left(\frac{N_D}{n_i}\right)$$

$$E_F = E_i - kT \ln\left(\frac{N_A}{n_i}\right)$$



温度越高，费米能级越接近本征费米能级

因为温度升高， n_i 降低，T对EF的影响小于 n_i 对EF的影响

简并掺杂半导体

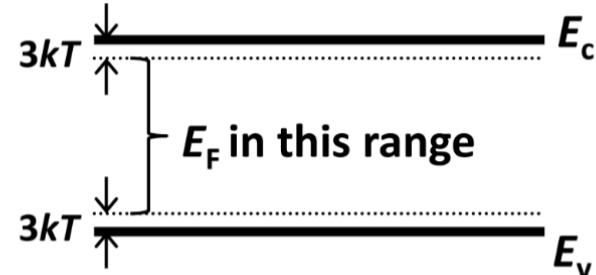
非简并掺杂半导体

轻掺杂半导体

➤ Recall that the expressions for n and p were derived using the Boltzmann approximation, i.e. we assumed:

- Electron and hole concentration are much lower than the effective density of states; $n, p \ll N_c, N_v$
- The distance among dopant atoms is large so as the interaction between them is negligible; 完全电离
- Impurities are usually fully ionized, i.e. $N_D \cong N_D^+ N_A \cong N_A^-$

$$E_v + 3kT \leq E_F \leq E_c - 3kT$$



The semiconductor is said to be **non-degenerately doped** in this case.

简并掺杂半导体

➤ If a semiconductor is very heavily doped, the Boltzmann approximation is not valid.

In Si at $T=300K$: $E_c - E_F < 3k_B T$ if $N_D > 1.6 \times 10^{18} \text{ cm}^{-3}$

$E_F - E_v < 3k_B T$ if $N_A > 9.1 \times 10^{17} \text{ cm}^{-3}$

The semiconductor is said to be **degenerately doped** in this case.

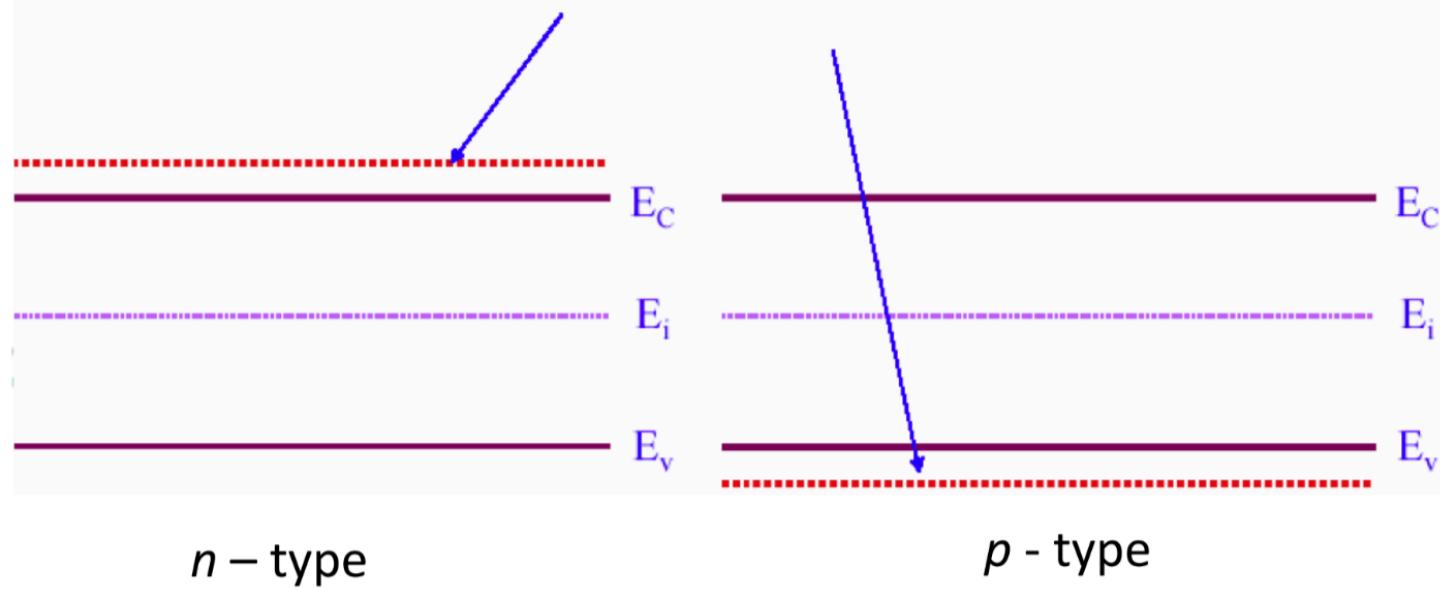
➤ Terminology:

“n+” → degenerately n-type doped. $E_F \cong E_c$

“p+” → degenerately p-type doped. $E_F \cong E_v$

简并掺杂半导体 继续掺杂

E_F will be above E_C or below E_V



掺杂浓度过高时，半导体带隙宽度可能发生变化

如果掺杂剂浓度占硅原子密度的很大一部分，则能带结构会受到扰动

- If the dopant concentration is a significant fraction of the silicon atomic density, the energy-band structure is perturbed → the band gap is reduced by ΔE_G :

