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### **Fundamentals of Solid State Physics**

## **Semiconductors - General**

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### **Further Reading**

- Ashcroft & Mermin, Chapter 28
- Solid State Electronic Devices by Streetman, Chap.3



### **Electronic Properties of Materials**







**Metal** 

**SiO** 



### Metal, Insulator, Semiconductor



Insulator

Semiconductor

Metal

### **Semiconductors - General Concepts**

- Band diagram E(k)
- Band gap  $E_g$
- Effective mass m\*
- Holes
- Density of States (DOS) g(E)
- Density of Carriers n<sub>c</sub> and p<sub>v</sub>
  - Mass Action Law
- Intrinsic and Extrinsic

### **Semiconductors - Applications**

### semiconductors are the basis of electronics and photonics



integrated circuits



LEDs



lasers





detectors

solar cells

### Semiconductor 半导体



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## Band Structure / Diagram 能带图

### Free electrons

energy



velocity

 $v = \frac{\hbar k}{m} = \frac{1}{\hbar} \frac{dE(k)}{dk}$ 

momentum



electron mass

$$\frac{1}{m} = \frac{1}{\hbar^2} \frac{d^2 E(k)}{dk^2}$$

*E-k* diagram (energy dispersion curve)

K

## Band Structure / Diagram 能带图

energy band gap

crystal momentum (*not* electron momentum)  $\hbar k$ 

 $E_{g}$ 

group velocity

$$v_g = \frac{1}{\hbar} \frac{dE(k)}{dk}$$

or

$$\mathbf{v} = \frac{1}{\hbar} \nabla_{\mathbf{k}} E(\mathbf{k})$$



*E-k* diagram (energy dispersion curve)

-

## Band Gap *E*<sub>g</sub>





$$E_{g} = 2V_{1}$$

Q: Why?

III	IV	V			H¢
5	6	7	8	9	10
B	C	N	0	F	Ne
13	14	15	16	17	18
Al	Si	P	S	CI	Ar
31	32	33	34	35	36
Ga	Ge	As	Se	Br	Kr
49	50	51	52	53	54
In	Sn	Sb	Te		Xe
81	82	83	84	85	86
TI	Pb	Bi	Po	At	Rn

### the nearly free electron model

#### at *T* = 300 K

	a (Å)	$E_{g}$ (eV)
C (diamond)	3.57	5.5
Si	5.43	1.1
Ge	5.66	0.66
α <b>-Sn</b>	6.49	0.08

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## Band Gap $E_g$



## Band Gap $E_g$

	$E_{g}$ (eV)		$E_g$ (eV)
Si	1.1	Ge	0.7
AIP	2.5	GaAs	1.4
MgS	4.0	ZnSe	3.5
NaCI	8.5	KBr	7.5



### Si < AIP < MgS < NaCl

Ge < GaAs < ZnSe < KBr

*more polarity -> larger V<sub>1</sub> -> larger E<sub>q</sub>* 

### **Direct and Indirect Gaps**



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Silicon - indirect

**GaAs - direct** 

### **Measurement of Band Gaps**



### **Measurement of Band Gaps**

# wavelength dependent optical absorption

#### Example: Zn<sub>2</sub>SnO<sub>4</sub> nanoparticles



### **Measurement of Band Gaps**



$$\left| E_g = \frac{hc}{\lambda_g} \right| \rightarrow$$

$$E(eV) = \frac{1240}{\lambda(nm)}$$

	${\it E}_g$ (eV)		
Si	1.1		
Ge	0.66		
GaAs	1.43		

#### effective mass

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E(k)}{dk^2}$$

The mass that an electron "seems" to have in a solid. It has nothing to do with the free electron mass  $m_0$ 

### For 3D solids, a tensor form



 $m^*$  is a function of k, can be smaller or larger than  $m_0$ , even can be negative

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## Effective Mass 有效质量

#### effective mass

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E(k)}{dk^2}$$

The mass that an electron "seems" to have in a solid. It has nothing to do with the free electron mass  $m_0$ 

For 3D solids, a tensor form

$$\frac{1}{\mathbf{M}_{ij}^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j}$$

 $m^*$  is a function of k, can be smaller or larger than  $m_0$ , even can be negative

$$m_0 = 9.11^{*}10^{-31} \text{ kg}$$
 20

Ea

The actual effective mass is a tensor, depending on the location  $(k_x, k_y, k_z)$ 



### **Approximation is taken for different calculations.**



The actual effective mass is a tensor, depending on the location  $(k_x, k_y, k_z)$ 





The actual effective mass is a tensor, depending on the location  $(k_x, k_y, k_z)$ 



close to band minimum parabolic approximation

$$E(k) \approx E_0 + \frac{\hbar^2}{2m^*} (k - k_0)^2$$

**3D DOS** 

$$g(E) = \frac{dn}{dE} = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} (E - E_0)^{1/2}$$

### Lecture Note 3.1

The actual effective mass is a tensor, depending on the location  $(k_x, k_y, k_z)$ 



### **Approximation is taken for different calculations:**

- Density of states calculations

$$g(E) = \frac{dn}{dE} = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} (E - E_0)^{1/2}$$

- Conductivity / mobility calculations

$$\sigma = ne\mu = ne^2 \frac{\tau}{m^*}$$

https://ecee.colorado.edu/~bart/book/effmass.htm 24

The actual effective mass is a tensor, depending on the location  $(k_x, k_y, k_z)$ 



### **Approximation is taken for different calculations.**

	Symbol	Germanium	Silicon	Gallium Arsenide
Smallest energy bandgap at 300 K	$E_g$ (eV)	0.66	1.12	1.424
Effective mass for density of states calculations				
Electrons	me*,dos/m0	0.56	1.08	0.067
Holes	mh*,dos/m0	0.29	0.57/0.811	0.47
Effective mass for conductivity calculations				
Electrons	me*,cond/m0	0.12	0.26	0.067
Holes	mh*,cond/m0	0.21	0.36/0.3861	0.34
Free electron mass	$m_0$ (kg)	ĩ	9.11 x 10 <sup>-31</sup>	

 Table 2.3.4
 Effective masses for both density of states and conductivity calculations.

effective mass

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E(k)}{dk^2}$$

### inverse curvature of the parabolic curve



effective mass





# We conventionally use *holes* to analyze the electron behaviors in VB



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hole is a quasi-particle (准粒子), different from positron (正电子)

# We conventionally use *holes* to analyze the electron behaviors in VB





air bubbles in water

In VB, properties of a hole compared to a missing electron in the same position of the band



Singleton, p45-p46



# Particles that conduct electrical current: electrons in CB and holes in VB



in CB

 $m_{e}^{*} > 0$ 



in VB



hole mobility

electron mobility





Particles that conduct electrical current: electrons in CB and holes in VB



$$\begin{vmatrix} \frac{\hbar^2}{2m} (k-g)^2 - E & -V_1 \\ -V_1 & \frac{\hbar^2}{2m} k^2 - E \end{vmatrix} = 0$$

$$\left[\frac{\hbar^2}{2m}(k-g)^2 - E\right]\left[\frac{\hbar^2}{2m}k^2 - E\right] - V_1^2 = 0$$

$$E_1(k), E_2(k)$$

Nearly Free electron ---->

$$V_1 \neq 0$$

and

$$V_1 \ll \frac{\hbar^2}{2m} \left(\frac{\pi}{a}\right)^2$$

$$\left[\frac{\hbar^2}{2m}(k-g)^2 - E\right] \left[\frac{\hbar^2}{2m}k^2 - E\right] - V_1^2 = 0$$

$$- E_{\pm}(k) = \frac{(A+B) \pm \sqrt{(A-B)^2 + 4V_1^2}}{2}$$

$$A = \frac{\hbar^2}{2m}k^2 \qquad B = \frac{\hbar^2}{2m}(k-g)^2$$

**Nearly Free electron** -

$$V_1 \neq 0$$
 and

$$V_1 \ll \frac{\hbar^2}{2m} \left(\frac{\pi}{a}\right)^2$$

$$\left[\frac{\hbar^2}{2m}(k-g)^2 - E\right] \left[\frac{\hbar^2}{2m}k^2 - E\right] - V_1^2 = 0$$

when  $k = \pi/a$ 

$$E_{+}\left(k = \frac{\pi}{a}\right) = \frac{\hbar^{2}}{2m}\left(\frac{\pi}{a}\right)^{2} + |V_{1}|$$
$$E_{-}\left(k = \frac{\pi}{a}\right) = \frac{\hbar^{2}}{2m}\left(\frac{\pi}{a}\right)^{2} - |V_{1}|$$



**Nearly Free electron**  $\longrightarrow$   $V_1 \neq 0$ 

$$\left[\frac{\hbar^2}{2m}(k-g)^2 - E\right] \left[\frac{\hbar^2}{2m}k^2 - E\right] - V_1^2 = 0$$

when  $k \sim \pi/a$ ,  $(A - B) \sim 0$ , take the first order approximation

$$E_{\pm}(k) = \frac{(A+B) \pm \sqrt{(A-B)^2 + 4V_1^2}}{2}$$

$$E_{\pm}(k) \approx \frac{A+B}{2} \pm V_1 \left[ 1 + \frac{1}{2} \frac{(A-B)^2}{4V_1^2} \right]$$

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$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E(k)}{dk^2}$$

$$\int \frac{m_e^*}{m_0} \approx \frac{1}{C/V_1 + 1}$$

$$\frac{m_h^*}{m_0} \approx \frac{1}{C/V_1 - 1}$$





For many semiconductors,  $V_1$  is very small ( $C/V_1 \sim 1-10$ )

$$m_e^* < m_h^* < m_0$$



- $m_e^*$  in CB is smaller than  $m_h^*$  in VB
- small V<sub>1</sub> ----> small m\* ----> large mobility μ



### **Examples**



(electrons have more freedom than holes)

### **Examples**

	a (Å)	E <sub>g</sub> (eV)	<b>m<sub>e</sub>* / m<sub>0</sub></b>	<i>m<sub>h</sub>* / m<sub>0</sub></i>	μ <sub>e</sub> (cm²/V/s)	μ <sub>h</sub> (cm²/V/s)
Si	5.43	1.1	0.26	0.38	1350	450
Ge	5.66	0.66	0.12	0.23	3900	1900
-	-	-	-	-	-	-
GaAs	5.65	1.42	0.067	0.45	8500	400
InAs	6.06	0.35	0.022	0.40	33000	450

\* effective mass for conductivity

- 1. large atoms ----> small V<sub>1</sub> ----> small E<sub>g</sub> ----> small  $m^*$  ----> large mobility  $\mu$
- 2.  $m_e^* < m_h^* < m_0$ 3.  $\mu_e^* > \mu_h^*$

### **Examples**

	a (Å)	E <sub>g</sub> (eV)	<b>m<sub>e</sub>* / m<sub>0</sub></b>	<i>m<sub>h</sub>* / m<sub>0</sub></i>	μ <sub>e</sub> (cm²/V/s)	$\mu_h$
Si	5.43	1.1	0.26	0.38	1350	450
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\* effective mass for conductivity

larger atoms
----> electrons have more freedom
----> smaller m\*, move faster



# Particles that conduct electrical current: electrons in CB and holes in VB



electrical conductivity

$$\sigma = n_c e \mu_e + p_v e \mu_h$$

**Q: How to calculate carrier densities?** 

 $n_c$  and  $p_v$  (#/cm<sup>3</sup>)

### **Band Diagram of Semiconductors**



The peaks and valleys of VB and CB can be approximately by *parabolic functions* 

## **Band Diagram of Semiconductors**



The peaks and valleys of VB and CB can be approximately by *parabolic functions* 

### **Q: How many electrons and holes?**

## Density of States (DOS) 态密度



## Density of States (DOS) 态密度



DOS - number of energy states/levels per unit energy in [*E*, *E*+*dE*], per unit volume



Density of electrons = DOS \* probability *f*  Density of holes = DOS \* (1-f)

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

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



### **Chemical Potential**



For pure semiconductors (intrinsic), the chemical potential  $\mu$  (Fermi level  $E_F$ ) lie within the band gap.

## Fermi Energy *E<sub>F</sub>* - A Little Note

In metals, Fermi energy/level  $E_F$  is the highest occupied state of electrons at T = 0 K.

In semiconductors, Fermi energy/level  $E_F$  is referred to the chemical potential  $\mu$ , which is inside the gap. No electrons at  $E_F$  !

"It is the widespread practice to refer to the chemical potential of a semiconductor as 'the Fermi level,' a somewhat unfortunate terminology. ... The term 'Fermi level' should be regarded as nothing more than a synonym for 'chemical potential,' in the context of semiconductors."

---- Ashcroft & Mermin, p573

### **Density of Carriers = DOS \* Probability**

### Intrinsic



#### electrons in CB

$$n_c = \int_{E_c}^{+\infty} g_c(E) \cdot f(E) dE$$

### If $\mu$ is in the gap, assume

$$E_c - \mu \gg k_B T$$

$$f(E) = \frac{1}{e^{(E-\mu)/k_BT} + 1}$$
$$\approx e^{-(E-\mu)/k_BT}$$

### holes in VB

$$p_{v} = \int_{-\infty}^{E_{v}} g_{v}(E) \cdot \left[1 - f(E)\right] dE$$

$$\mu - E_v \gg k_B T$$

$$1 - f(E) = \frac{1}{e^{(\mu - E)/k_B T} + 1}$$
$$\approx e^{-(\mu - E)/k_B T}$$

Non-Degenerate semiconductors (非简并半导体): Fermi-Dirac is approximated by Maxwell-Boltzmann distribution not valid for high temperature or small band gap

### electrons in CB

$$\begin{aligned} n_{c} &= \int_{E_{c}}^{+\infty} g_{c}(E) \cdot f(E) dE \\ &= \int_{E_{c}}^{+\infty} \frac{1}{2\pi^{2}} \left( \frac{2m_{e}^{*}}{\hbar^{2}} \right)^{3/2} (E - E_{c})^{1/2} \cdot e^{-(E - \mu)/k_{B}T} dE \\ &= \frac{1}{4} \left( \frac{2m_{e}^{*} k_{B}T}{\pi \hbar^{2}} \right)^{3/2} e^{-(E_{c} - \mu)/k_{B}T} \\ &= N_{c}(T) e^{-(E_{c} - \mu)/k_{B}T} \end{aligned}$$

$$N_{c}(T) = \frac{1}{4} \left( \frac{2m_{e}^{*}k_{B}T}{\pi\hbar^{2}} \right)^{3/2} = 2.5 \left( \frac{m_{e}^{*}}{m_{0}} \right)^{3/2} \left( \frac{T}{300 \text{ K}} \right)^{3/2} \times 10^{19} \text{ cm}^{-3}$$

note here we use the integral

$$\int_{0}^{+\infty} x^{1/2} \cdot e^{-x/a} dx = \frac{\sqrt{\pi}}{2} a^{3/2}$$

**SO** 

$$\int_{E_c}^{+\infty} (E - E_c)^{1/2} \cdot e^{-(E - \mu)/k_B T} dE$$
$$= \frac{\sqrt{\pi}}{2} (k_B T)^{3/2} e^{-(E_c - \mu)/k_B T}$$

#### holes in VB

$$p_{\nu} = \int_{-\infty}^{E_{\nu}} g_{\nu}(E) \cdot [1 - f(E)] dE$$
  
=  $\int_{-\infty}^{E_{\nu}} \frac{1}{2\pi^{2}} \left(\frac{2m_{h}^{*}}{\hbar^{2}}\right)^{3/2} (E_{\nu} - E)^{1/2} \cdot e^{-(\mu - E)/k_{B}T} dE$   
=  $\frac{1}{4} \left(\frac{2m_{h}^{*}k_{B}T}{\pi\hbar^{2}}\right)^{3/2} e^{-(\mu - E_{\nu})/k_{B}T}$   
=  $P_{\nu}(T)e^{-(\mu - E_{\nu})/k_{B}T}$ 

$$P_{v}(T) = \frac{1}{4} \left( \frac{2m_{h}^{*}k_{B}T}{\pi\hbar^{2}} \right)^{3/2} = 2.5 \left( \frac{m_{h}^{*}}{m_{0}} \right)^{3/2} \left( \frac{T}{300 \text{ K}} \right)^{3/2} \times 10^{19} \text{ cm}^{-3}$$

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effective density of states (有效态密度) no physical meaning, just two constants



Ε when T > 0 K  $n_{c} = N_{c}(T)e^{-(E_{c}-\mu)/k_{B}T} > 0$ ► **k**  $p_v = P_v(T)e^{-(\mu - E_v)/k_BT} > 0$ 

#### conductivity

$$\sigma = n_c e \mu_e + p_v e \mu_h$$

T > 0 K thermalization 热激发 **CB and VB are partly filled** conductor



at equilibrium,  $n_c p_v$  is a constant

### **Carriers in Semiconductors**

- For calculations here, we go back to classical physics, assume:
  - Carriers are much fewer than DOS



- Carriers are non-Degenerate (Boltzmann Distribution)
- □ Carriers are almost in the same energies ( $E_c$  and  $E_v$ )
- Carriers have the same velocities and motilities

$$\sigma = n_c e \mu_e + p_v e \mu_h$$



## Mass Action Law - A Little Notion

The product of electron and hole concentrations is a constant, at a fixed temperature

$$n_c p_v = n_i^2 = N_v(T) P_v(T) e^{-E_g/k_B T}$$

In water, the product of H<sup>+</sup> and OH<sup>-</sup> concentrations is also a constant

$$[H^+][OH^-] = K_w = 10^{-14} (mol/L)^2 (at 25 °C)$$

Both are originated from classical statistics (nondegenerate, Maxwell-Boltzmann distribution), not related to quantum mechanics

## Thank you for your attention