半導體元件與物理
Semiconductor Devices and physics
許正興
國立聯合大學電機工程學系
1. Crystal Structure of Solids
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3. Semiconductor in Equilibrium and Carrier Transport phenomena
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Part II

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In this chapter, we will generalize these concepts to the electron in a crystal lattice. One of our goals is to determine the electrical properties of a semiconductor material, which we will then use to develop the current-voltage characteristics of semiconductor devices. To determine the properties of electrons in a crystal lattice, and to determine the statistical characteristics of the very large number of electrons in a crystal.

**Allowed and Forbidden Energy Bands**

Only discrete values of electron energy are allowed. The radial probability density for the electron was also determined. This function gives the probability of finding the electron at a particular distance from the nucleus and shows that the electron is not-localized at a given radius. Apply quantum mechanics and Schrödinger’s wave equation to the problem of an electron in a single crystal. We find that the electronic energy states occur in bands of allowed states that are separated by forbidden energy bands.
Formation of Energy Band

Figure (a) shows the radial probability density function for the lowest electron energy state of the single, noninteracting hydrogen atom, figure (b) shows the same probability curves for two atoms that are in close proximity to each other. The wave functions of the two atom electrons overlap, which means that the two electrons will interact. → this interaction or perturbation results in the discrete quantized energy level splitting into two discrete energy levels, schematically shown in figure (c). → the splitting of the discrete state into two states is consistent with the Pauli exclusion principle.

(a) $p(r)$

(b) $p(r)$

(c) $n = 1$
A regular periodic arrangement of hydrogen-type atoms that are initially very far apart, and begin pushing the atoms together, the initial quantized energy level will split into a band of discrete energy levels. At the equilibrium interatomic distance \( (r_0) \), there is a band of allowed energies, but within the allowed band, the energies are at discrete levels. The Pauli exclusion principle states that the joining of atoms to form a system (crystal) does not alter the total number of quantum states regardless of size.

\[ \rightarrow \] Since no two electrons can have the same quantum number, the discrete energy must split into a band of energies in order that each electron can occupy a distinct quantum state.
Consider again a regular periodic arrangement of atoms, in which each atom now contains more than one electron. Suppose the atom in this imaginary crystal contains electrons up through $n = 3$ energy level. If the atoms are initially very far apart, the electrons in adjacent atoms will not interact and will occupy the discrete energy level. If these atoms are brought closer together, the outermost electrons in the $n = 3$ energy shell will begin to interact initially, so that this discrete energy level will split into a band of allowed energies. If the atoms continue to move closer together, the electrons in the $n = 2$ shell may begin to interact and will also split into a band of allowed energies. Finally, if the atoms become sufficiently close together, the innermost electrons in $n = 1$ level may interact, so that this energy level may also split into a band of allowed energies.

If the equilibrium interatomic distance is $r_o$, then we have bands of allowed energies that the electrons may occupy separated by bands of forbidden energies.

Those definitions is the energy-band theory of single-crystal materials.
(a) Schematic representation of an isolated silicon atom. (b) the splitting of the 3s and 3p states of silicon into the allowed and forbidden energy bands.

=> As the interatomic distance decreases, the 3s and 3p states interact and overlap. At the equilibrium interatomic distance, the bands have again split, but now four quantum states per atom are in the lower band and four quantum states per atom are in the upper band. ⇒ At absolute zero degrees, electrons are in the lowest energy state, so that all states in the lower band (the valence band) will be full and all state in the upper band (conduction band) will empty. ⇒ the bandgap energy $E_g$ between the top of the valence band and the bottom of the conduction band is the width of the forbidden energy band.
The Kronig-Penney Model

The potential function of a single, noninteracting, one-electron atom is shown in Fig. a. Also indicated on the figure are the discrete energy levels allowed for the electron. Fig. b shows the same type of potential function for the case when several atoms are in close in a 1-D array.

The potential functions of adjacent atoms overlap, and the net potential function for this case is shown in fig. c.

It is this potential function we would need to use in Schrodinger’s wave equation to model a 1-D single-crystal material.
The solution to Schrödinger’s wave equation, for 1-D single-crystal lattice, is made more tractable by considering a simpler potential function.

→ Figure is the 1-D Kronig-Penney model of the periodic potential function, which is used to represent a 1-D single-crystal lattice.

→ we need to solve Schrödinger’s wave equation in each region. As with previous quantum mechanical problems, the more interesting solution occurs for the case when $E<V_0$, which corresponds to a particle being bound within the crystal. ➞ the electrons are contained in the potential wells, but we have the possibility of tunneling between wells. ➞ the Kronig-Penney model is an idealized periodic potential representing a 1-D single crystal, but the results will illustrate many of the important features of the quantum behavior of electrons in a periodic lattice.
The K-space Diagram

From solve Schrodinger’s wave function with differential the Kronig-Penney model defined region, we find the relation between the parameter $k$ (constant of motion), total energy $E$ and the potential barrier $bV_0 \rightarrow P'(\sin \alpha a/a) + \cos \alpha a = \cos k a$; but note that equation is not a solution of Schrodinger’s wave function but gives the conditions for which Schrodinger’s wave function will have a solution.

To begin to understand the nature of the solution, initially consider the special case for which $V_0 = 0$. In the case $P' = 0$, which corresponds to a free particle since there are no potential barrier. $\rightarrow \cos \alpha a = \cos ka$ or $\alpha = k$

$\rightarrow$ Since the potential is equal to zero, the total energy $E$ is equal to the kinetic energy, so that $\rightarrow$

$$\alpha = \sqrt{\frac{2mE}{\hbar^2}} = \sqrt{\frac{2m(\frac{1}{2}mv^2)}{\hbar^2}} = \frac{p}{\hbar} = k$$

where $p$ is the particle momentum
The constant of motion parameter $k$ is related to the particle momentum for the free electron. The parameter $k$ is also referred to as a wave number $\tilde{k}$.

Relate the energy and momentum as

$$E = \frac{p^2}{2m} = \frac{k^2 \hbar^2}{2m}$$

Figure shows the parabolic relation of above equation between the energy $E$ and momentum $p$ for the free particle since the momentum and wave number are linearly related, figure is also the $E$ versus $k$ curve for the free particle.

Consider the relation between $E$ and $k$ from above equation for the particle in the single-crystal lattice. As the parameter $P'$ increases, the particle becomes more tightly bound to the potential well or atom.

we may define the left side of the above equation to be a function $f(\alpha a)$

$$f(\alpha a) = P' \sin \alpha a + \cos \alpha a$$

#### Figure 3.7 自由電子的 $E - k$ 拋物曲線圖。
Figure a is a plot of the first term of above equation versus \( \alpha a \). Figure b shows a plot of the \( \cos \alpha a \) term and figure c is the sum of the two terms.

\[
f(\alpha a) = \cos k\alpha
\]
Figure shows this plot and shows the concept of allowed energy bands for the particle propagating in the crystal lattice. Since $E$ has discontinuities, we also have the concept of forbidden energies for the particles in the crystal.
Consider again the right side of above equation, which is the function \( \cos ka \).

\[
\cos ka = \cos (ka + 2n\pi) = \cos (ka - 2n\pi)
\]

where \( n \) is a positive integer.

Figure (left) shows how various segments of the curve can be displaced by \( 2\pi \) factor. Figure (right) shows the case in which the entire \( E \) versus \( k \) plot is contained within \(-\pi/a < k < \pi/a\). This plot is referred to as a reduced \( k \)-space diagram, or reduced-zero representation.
Electrical Conduction in Solids

We are interested in determining the current-voltage characteristics of semiconductor devices. We will need to consider electrical conduction in solid as it relates to the band theory we have just developed. We begin by considering the motion of electrons in the various allowed energy bands.

The energy band and the bond model

2-D representation of the covalent bonding in a semiconductor at T = 0 K.

All of the valence electrons are in the valence band. The upper energy band, the conduction band, is completely empty at T = 0 K.
As the temperature increases above 0 K, a few valence band electrons may gain enough thermal energy to break the covalent bond and jump into the conduction band. → Figure a shows a 2-D representation of this bond-breaking effect and figure b, a simple line representation of the energy-band model, shows the same effect.

The semiconductor is neutrally charged. This means that as the negatively charged electron breaks away from its covalent bonding position, a positively charged “empty state” is created in the original covalent bonding position in the valence band. → as the temperature further increases, more covalent bands are broken, more electrons jump to the conduction band, and more positive “empty states” are created in the valence band.
We can also relate this bond breaking to the E versus k energy bands. Figure a shows the E versus k diagram of the conduction and valence bands at $T = 0$ K. The energy states in the valence band are completely full and the states in the conduction band are empty. => Figure b shows these same bands for $T > 0$ K, in which some electrons have gained enough energy to jump to the conduction band and have left empty states in the valence band.
**Drift current**

Current is due to the net flow of charge. If we had a collection of positively charged ions with a volume density $N$ (cm$^{-3}$) and an average drift velocity $v_d$ (cm/s), then the drift current density would be

$J = qNv_d$  A/cm$^2$

If, instead of considering the average drift velocity, we considered the individual ion velocities, then we would write the drift current density as

$J = q \sum_{i=1}^{N} v_i$

where $v_i$ is the velocity of the $i$th ion.

Since electrons are charged particles, a net drift of electrons in the conduction band will give rise to a current. The electron distribution in the conduction band is an even function of $k$ when no external force is applied. Recall that $k$ for a free electron is related to momentum so that, since there are as many electrons with a $+|k|$ value as there are with a $-|k|$ value, the net drift current density due to these electrons is zero — certainly expected since there is no externally applied force.

If a force is applied to particle and the particle moves, it must gain energy.

$dE = F \, dx = Fv \, dt$ — if an external force is applied to the electrons in the conduction band, there are empty energy states into which the electrons can move; therefore, because of the external force, electrons can gain energy and a net momentum.
The electron distribution in the conduction band may look like as figure.

→ The drift current density due to the motion of electron as

\[ J = -e \sum_{i=1}^{n} v_i \]
Electron effective mass

The movement of an electron in a lattice will be different from that of an electron in free space. \[ \mathbf{F}_{\text{total}} = \mathbf{F}_{\text{ext}} + \mathbf{F}_{\text{int}} = ma \]

where internal force due to positively charged ions or protons and negatively charged electrons; \(a\) is acceleration and \(m\) is the rest mass of the particle. \(\Rightarrow\) since it is difficult to take into account all of the internal forces:

\[ \mathbf{F}_{\text{ext}} = m^*a \]

where the acceleration \(a\) is now directly related to the external force, the parameter \(m^*\) called the effective mass, takes into account the particle mass and also takes into account the effect of the internal force.

\[ \Rightarrow \quad \frac{1}{\hbar} \frac{dE}{dk} = \frac{p}{m} = \nu \]

= take the second derivative

\[ \frac{d^2E}{dk^2} = \frac{\hbar^2}{m} \]

\[ \Rightarrow \quad \frac{1}{\hbar^2} \frac{d^2E}{dk^2} = \frac{1}{m} \]

The energy near the bottom of this energy band may be approximated by a parabola. The energy \(E_c\) is the energy at the bottom of the band.
Concept of Hole

When a valence electron was elevated into the conduction band, a positively charged “empty state” was created. → if a valence electron gains a small amount of thermal energy, it may hop into the empty state. → the movement of a valence electron into the empty state is equivalent to the movement of the positively charge empty state itself.

→ Following figure show that the movement of valence electrons in the crystal alternately filling one empty state and creating a new empty state, a motion equivalent to a positive charge moving in the valence band. → the crystal now has a second equally important charge carrier that can give rise to a current. → this charge carrier is called a hole.
The drift current density due to electrons in the valence band, can be written as

\[ J = -e \sum_{i\text{(filled)}} v_i \]

where the summation extends over all filled states. 

⇒ This summation is inconvenient since it extends over a nearly full valence band and takes into account a very large number of states. 

\[ J = -e \sum_{i\text{(total)}} v_i + e \sum_{i\text{(empty)}} v_i \]

⇒ If we consider a band that is totally full, all available states are occupied by electrons. The individual electrons can be thought of as moving with a velocity as given 

\[ v(E) = \left( \frac{1}{\hbar} \right) \left( \frac{dE}{dk} \right) \]

⇒ The band is symmetric in \( k \) and each state is occupied so that, for every electron with a velocity \( |v| \), there is a corresponding electron with a velocity \(-|v|\). Since the band is full, the distribution of electrons with respect to \( k \) cannot be changed with an externally applied force. 

⇒ the net drift current density generated from a completely full band, then, is zero, or

\[ -e \sum_{i\text{(total)}} v_i = 0 \]

⇒ the drift current density for an almost full band is

\[ J = +e \sum_{i\text{(empty)}} v_i \]
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$$v(E) = \left(\frac{1}{\hbar}\right) \left(\frac{dE}{dk}\right)$$

The band is symmetric in $k$ and each state is occupied so that, for every electron with a velocity $|v|$, there is a corresponding electron with a velocity $-|v|$. Since the band is full, the distribution of electrons with respect to $k$ cannot be charged with an externally applied force. The net drift current density generated from a completely full band, then, is zero, or

$$-e \sum_{i\text{(total)}} v_i \equiv 0$$
The drift current density for an almost full band as

\[ J = +e \sum_{i(\text{empty})} v_i \]

Above equation to placing a positively charged particle in the empty states and assuming all other states in the band are empty, or neutrally charged.

⇒ The energy near the top of the allowed energy band \( E_v \) may again be approximated by a parabola so that we may write

\[ (E - E_v) = -C_2(k)^2 \]

⇒ take the second derivative

\[ \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} = -2C_2 \Rightarrow \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} = \frac{-2C_2}{\hbar^2} \]

\[ \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} = \frac{-2C_2}{\hbar^2} \]

(a) 負電荷具備傳統方式表示的電子填滿狀態及空缺狀態；(b) 正電荷佔

據原本空缺狀態的觀念。
Metal, insulators, and semiconductors

(a) 允許能帶（空的）

(b) 允許能帶（滿的）

(c) 介電帶（空的）

許能帶為：(a)一個空的能帶；(b)一個完全填滿的能帶；(c)兩個允許能帶之間的能隙。
允許能帶為：(a)一個幾乎空缺的能帶；(b)一個幾乎填滿的能帶；(c)兩個允許能帶間的能隙。

金屬的兩種可能能帶：(a)部分填滿的能帶；(b)重疊的允許能帶。
Extension to three dimensions

The basic concept of allowed and forbidden energy bands and the basic concept of effective mass have been developed in the last sections. And it also should be extend these concepts to 3-D and real crystals. → we will qualitatively consider particular characteristics of the 3-D crystal in terms of the E versus k plots, bandgap energy and effective mass.

→ The potential function to a 3-D crystal is that the distance between atoms varies as the direction through the crystal changes. → Electrons traveling in different directions encounter different potential patterns and therefore different $k$-space boundaries. (in figure). The $E$ versus $k$ diagrams are in general a function of the $k$-space direction in a crystal.
Show different crystal directions.

(a) arsenic; and (b) silicon band structures.

\[ \Delta E = 0.31\]
Density of States Function

Since current is due to the flow of charge, an important step in the process is to determine the number of electrons and holes in the semiconductor that will be available for conduction. The number of carriers that can contribute to the conduction process is a function of the number of available energy or quantum states since, by the Pauli exclusion principle, only one electron can occupy a given quantum state. We discussed the splitting of energy levels into bands of allowed and forbidden energies, we indicated that the band of allowed energies was actually made up of discrete energy levels density of these allowed energy states as a function of energy in order to calculate the electron and hole concentrations.
Mathematical Derivation

To determine the density of allowed quantum states as a function of energy, we need to consider an appropriate mathematical model. → Electrons are allowed to move relatively freely in the conduction band of a semiconductor, but are confined to the crystal. → As a first step, consider a free electron confined to a three-dimensional infinite potential well, where the potential well represent the crystal. =>

\[ V(x, y, z) = 0 \quad \text{for} \quad 0 < x < a \]
\[ 0 < y < a \]
\[ 0 < z < a \]
\[ V(x, y, z) = \infty \quad \text{elsewhere} \]

where the crystal is assumed to be a cube with length \( a \)

Schrodinger’s wave equation in 3-D can be solved using the separation of variables technique.

\[ \frac{2mE}{\hbar^2} = k^2 = k_x^2 + k_y^2 + k_z^2 = (n_x^2 + n_y^2 + n_z^2) \left( \frac{\pi^2}{a^2} \right) \]

where \( n_x, n_y, n_z \) are positive integers
We can schematically plot the allowed quantum states in $k$ space. Figure shows a 2-D plot as a function of $k_x$ and $k_y$. Each point represents an allowed quantum state corresponding to various integral values of $n_x$ and $n_y$ positive and negative values of $k_x$, $k_y$, $k_z$ have the same energy and represent the same energy state, but the density of quantum states will be determined by considering only the positive one-eighth of the spherical $k$ space.

The distance between two quantum states in the $k_x$ direction, for example, is given by

$$k_{x+1} - k_x = (n_x + 1)\left(\frac{\pi}{a}\right) - n_x\left(\frac{\pi}{a}\right) = \frac{\pi}{a}$$

Generalizing this result to 3-D, the $V_k$ of a single quantum states is

$$V_k = \left(\frac{\pi}{a}\right)^3$$

A differential volume in $k$ space and is given by $4\pi k^2 dk$, so the differential density of quantum states in $k$ space can be written as

$$g_T(k) dk = 2\left(\frac{1}{8}\right)\cdot\frac{4\pi k^2}{\left(\frac{\pi}{a}\right)^3}$$

(a) 在 $k$ 空間中，二維的允許量子狀態陣列；(b) 正的八分之一的球形 $k$ 空間。
The first factor, 2, takes into account the two spin states allowed for each quantum state; the next factor, \( (1/8) \), takes into account that we are considering only the quantum states for positive values of \( k_x, k_y, \) and \( k_z \). \[ g_T(k) \, dk = \frac{\pi k^2 \, dk}{\pi^3} \cdot a^3 \]

\( \Rightarrow \) Above equation gives the density of quantum states as a function of momentum, through the parameter \( k \). \( \Rightarrow \) for a free electron, the parameters \( E \) and \( k \) are related by

\[ k^2 = \frac{2mE}{\hbar^2} \quad \text{or} \quad k = \frac{1}{\hbar} \sqrt{2mE} \quad \text{The differential} \quad dk \quad \text{is} \quad dk = \frac{1}{\hbar} \sqrt{2E} \, dE \]

Substituting above parameter to above equation, the number of energy states between \( E \) and \( E + dE \) is given by

\[ g_T(E) \, dE = \frac{\pi a^3}{\pi^3} \left( \frac{2mE}{\hbar^2} \right) \cdot \frac{1}{\hbar} \sqrt{ \frac{m}{2E} } \, dE \]

\( \Rightarrow \) Since \( \hbar = h / 2\pi \) \( \Rightarrow \)

Above equation gives the total number of quantum states between the energy \( E \) and \( E + dE \) in the crystal space volume of \( a^3 \). \( \Rightarrow \) If we divide by the volume \( a^3 \), then the density of quantum states per unit volume of the crystal \( \Rightarrow \)

The density of quantum states is a function of energy \( E \). as the energy of this free electron becomes small, the number of available quantum states decreases.
Extension to Semiconductors

The parabolic relationship between energy and momentum of a free electron was given as \( E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \) \( \Rightarrow \) the \( E \) versus \( k \) curve near \( k=0 \) at the bottom of the conduction band can be approximated as a parabola \( \Rightarrow \) so we may \( \Rightarrow E - E_c = \frac{\hbar^2 k^2}{2m_n^*} \) of allowed electronic energy states in the conduction band as \[ g_c(E) = \frac{4\pi (2m_n^*)^{3/2}}{\hbar^3} \sqrt{E - E_c} \quad E \geq E_c \]

The density of quantum states in the valence band can be obtained by using the same infinite potential well model \( \Rightarrow \) since the hole is also confined in the semiconductor crystal and can be treated as a “free” particle. \( \Rightarrow \) approximate the \( E \) versus \( k \) curve near \( k=0 \) \( \Rightarrow E = E_v - \frac{\hbar^2 k^2}{2m_p^*} \) \( \Rightarrow E_v - E = \frac{\hbar^2 k^2}{2m_p^*} \)

\( \Rightarrow \) The density of states function to apply to the valence band \[ g_v(E) = \frac{4\pi (2m_p^*)^{3/2}}{\hbar^3} \sqrt{E_v - E} \quad E \leq E_v \]

The forbidden energy band, so \( g(E) = 0 \) for \( E_v < E < E_c \).
Statistical Mechanics

Fermi-Dirac Probability Function

In determining the statistical behavior of particles, we must consider the laws that the particles obey. The Fermi-Dirac probability function, the particles are again indistinguishable, but now only one particle is permitted in each quantum state, electrons in a crystal obey this law. → the particles are assumed to be noninteracting.

We may write the most probable distribution function as

$$\frac{N(E)}{g(E)} = f_F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

Where $E_F$ is called the Fermi energy. The number density $N(E)$ is the number of particles per unit volume per unit energy and the function $g(E)$ is the number of quantum states per unit volume per unit energy. → The function $f_F(E)$ is called the Fermi-Dirac distribution or probability function and gives the probability that a quantum states at the energy $E$ will be occupied by an electron.
The Distribution Function and the Fermi Energy

To begin to understand the meaning of the distribution function and the Fermi energy, we can plot the distribution function versus energy.

\[ N(E) \quad g(E) = f_F(E) = \frac{1}{1 + \exp \left( \frac{E - E_F}{kT} \right)} \]

\[ \Rightarrow \exp[(E-E_F)kT] \rightarrow \exp(-\infty) = 0 \Rightarrow f_F(E<E_F) = 1 \]

\[ \Rightarrow \text{let } T=0 \text{ K and } E>E_F \Rightarrow \exp[(E-E_F)kT] \rightarrow \exp(+\infty) \rightarrow +\infty \Rightarrow f_F(E>E_F) = 0 \]

The Fermi-Dirac distribution function for \( T = 0 \text{ K} \) is plotted in Figure.

\[ f_F(E) \]

\[ T=0 \text{ K} \]

- 1. for \( T = 0 \text{ K} \), the electrons are in their lowest possible energy states
- 2. probability of a quantum state being occupied is unity for \( E<E_F \) and the probability of a state being occupied is zero for \( E>E_F \)
- 3. All electrons have energies below the Fermi energy at \( T = 0 \text{ K} \)
Left figure shows discrete energy levels of a particular as well as the number of available quantum at each energy ($T = 0 \, \text{K}$). → the electrons will be in the lowest possible energy state → the probability of a quantum state being occupied in energy levels $E_1$ through $E_4$ is unity; probability of a quantum state being occupied in energy levels $E_5$ is zero. => for $T > 0 \, \text{K}$, (as shows in right figure), several electrons from the $E_4$ have gained enough energy to jump to $E_5$ and from $E_3$ has jumped to $E_4$. → As the temperature changes, the distribution of electrons versus energy changes.

The density of quantum states $g(E)$ is a continuous function of energy as middle figure. If we have $N_0$ electrons in this system, then the distribution of these electrons among the quantum states at $T = 0 \, \text{K}$ is shown by the dashed line. The electrons are in the lowest possible energy state so that all states below $E_F$ are filled and all states above $E_F$ are filled and all states above $E_F$ are empty. → If $g(E)$ and $N_0$ are known for this particular system, then the Fermi energy $E_F$ can be determined
The change in the electron distribution among energy levels for $T > 0$ K can be seen by plotting the Fermi-Dirac distribution function. → If we let $E = E_F$ and $T > 0$ K,

$$f_{F}(E = E_{F}) = \frac{1}{1 + \exp (0)} = \frac{1}{1 + 1} = \frac{1}{2}$$

=> the probability of a state being occupied at $E = E_F$ is $1/2$.

→ Fermi energy is independent of temperature.

不同溫度的費米機率函數對能量的關係。
We note that the probability of a state a distance \( dE \) above \( E_F \) being occupied is the same as the probability of a state a distance \( dE \) below \( E_F \) being empty → the function \( f_F(E) \) is symmetrical with the function \( 1-f_F(E) \) about the Fermi energy, \( E_F \).

\[
f_F(E) \approx \exp\left[-\frac{(E - E_F)}{kT}\right]
\]

Consider the case when \( E-E_F>>kT \), where the exponential term in the denominator of above equation is much greater than unity → neglect the 1 in the denominator, so that Fermi-Dirac distribution function becomes:

\[
f_F(E) \approx \exp\left[-\frac{(E - E_F)}{kT}\right]
\]
聯大電機系 電子材料與元件應用實驗室