Fundamentals of Semiconductors for Energy Harvesting

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Abstract The most important feature of a semiconductor for the purpose of energy harvesting, such as photovoltaic cells and photocatalysts, is that the number densities of electrons and holes in a semiconductor is much smaller than in a metal and those densities can be easily altered by external excitation such as light irradiation. From a thermodynamic viewpoint, even though the internal energies of electrons and holes are fixed at the band-edge energies of the conduction and the valance bands, respectively, their *free energies*, which is equivalent to quasi Fermi levels, can be altered significantly by the logarithm of electron/hole density. The larger density of electrons (holes) reduces their entropy and their free energy gets closer to the internal energy, i.e., the conduction (valence) band edge energy. The free energy difference between electrons and holes in a semiconductor is the potential to exert work externally, and it corresponds to the terminal voltage for a photovoltaic cell. Such accumulation of electrons and holes upon the absorption of photons is the common working principle for photovoltaic cells and photocatalysts. The following properties are therefore important for a semiconductor to serve as a good material for photovoltaic cells and photocatalysts:

(1) strong light absorption per volume;
(2) slow recombination between electrons and holes, which necessitates as small density of crystal defects as possible not only inside the semiconductor but also at the surface;
(3) efficient transport of electrons and holes to different regions that accepts electrons or holes selectively.

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M. Sugiyama et al. (eds.), *Solar to Chemical Energy Conversion*,
Lecture Notes in Energy 32, DOI 10.1007/978-3-319-25400-5_3

1 Electrons and Holes in a Semiconductor

A characteristic of a semiconductor is the existence of bands as a result of hybridization among the orbitals with valence (highest energy) electrons as shown in Fig. 1. It should be emphasized that a band is the collection of quantum states, the wave function of which spreads over an entire crystal. Fermi-Dirac distribution of electrons in the bands, which is a thermodynamic principle as will be described in Sect. 8, makes one of the bands in a semiconductor, which is called as the valence band, almost fully occupied by electrons and another band just above the valence band is made almost empty and it is called as the conduction band. At a temperature higher than zero kelvin, for the sake of minimizing the total free energy of the system, some electrons occupy the states in the conduction band and correspondingly some vacant states exist in the valence band. An electron surrounded by unoccupied states in the conduction band move among neighboring quantum states upon external force, which is the quantum-mechanical view of electrons' motion in a semiconductor. Similarly, a vacancy in the valence band, which is surrounded by the states occupied by electrons, switch from a state to a neighboring one upon external force; this is the quantum-mechanical view of holes' motion. For electrons and holes to achieve equilibrium in a certain spatial range of a semiconductor, they have to migrate in the range. For the thermodynamics of electrons and holes in a semiconductor, therefore, our interest is focused on the electrons and holes that can move spatially. Those mobile electrons and holes are often referred to as *carriers* since they carry charges. This is why we focus on a smaller number of electrons in the conduction band and neglect abundant electrons in the lower-energy bands including the valence band. In the same manner, we focus on a small number of holes in the valance band and neglect all the vacant quantum states that exist in the conduction band and the bands with higher energies.

A characteristic of semiconductors is that the concentrations of electrons and holes can be altered by doping. In this chapter, we refer to concentration as the

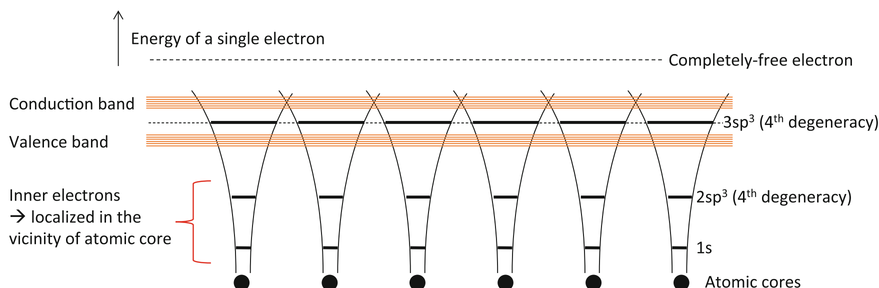

Fig. 1 A schematic energy diagram of atomic quantum states and bands in a silicon crystal. One s- and three p- orbitals form four degenerated sp^3 hybrid orbitals. The orbitals with the highest energy (sp^3) interfere with each other due to the spatial overlap of orbitals and a set of stabilized states (the valance band) and un-stabilized states (the conduction band) are formed

number density in a unit volume. Fermi-Dirac distribution of electrons imposes a law of mass action in which the product between electron concentration n and hole concentration p is determined by several material parameters as well as temperature,

$$np = N_c N_v \exp\left(-\frac{E_g}{kT}\right), \tag{1}$$

where N_c (N_v) are the effective density of states in the conduction (valance) band, E_g is the bandgap, k is the Boltzmann constant and T is absolute temperature. Approximately, the effective density of states for electrons (holes) in the conduction (valence) band is the maximum number of quantum states that electrons (holes) can occupy. It is, as well as the bandgap, a parameter unique to a semiconductor material. For example, the values for GaAs at 300 K is as follows: $N_c = 4.7 \times 10^{17}$ cm^{-3}, $N_v = 9.0 \times 10^{18}$ cm^{-3} and $E_g = 1.42$ eV, resulting in the concentrations of electrons n and holes p if no impurity exist, $n = p$=4.7 × 10^6 cm^{-3}. The value is called intrinsic carrier concentration n_i where "intrinsic" means a pure semiconductor without any impurity.

The relationship in Eq. (1) also holds true when dopant atoms exist in a semiconductor. Adding atoms with extra valance electrons to a semiconductor (n-type doping) increases the concentration of electrons according to the concentration of dopant atoms, and the concentration of holes decreases to keep the relationship in Eq. (1) as depicted in Fig. 2. Similarly, the dopant atoms with insufficient valance electrons increases the concentration of holes (p-type doping) and the concentration

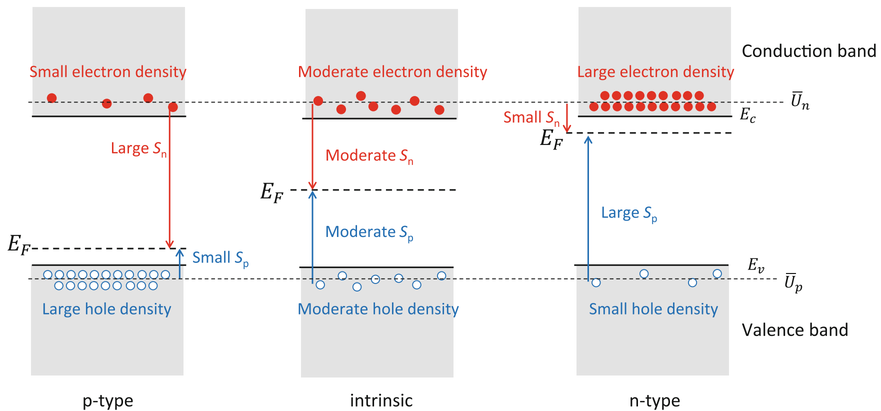

Fig. 2 Concentrations of electrons and holes in a semiconductor with different doping conditions. The relevant energies are also shown; E_c the conduction-band edge, E_v the valence-band edge, E_F the Fermi level (for both electrons and holes), $\bar{U}_n$ the averaged internal energy of elctrons, $\bar{U}_p$: the averaged internal energy of holes. S_n denotes entropy for electrons and S_p is entropy for holes

of electrons decreases accordingly. Such an interaction between the concentrations means equilibrium between electrons and holes. The situation is analogous to H^+ and OH^- ions in an electrolyte.

2 Free Energy of Electrons in a Semiconductor: An Intuitive Picture

A variety of semiconductor heterostructures can be fabricated by combining semiconductors with different bandgaps and doping concentrations. A typical example of a silicon pn junction is shown in Fig. 3. It should be emphasized that a n-type-doped semiconductor contains the same density of free electrons and positive ions of dopant atoms, resulting in the neutral charge density. The ions are bound to the lattice of silicon atoms. Similarly, a p-type semiconductor contains both free holes and negative ions of dopant atoms. At the pn junction, electrons and holes migrate and combine with each other, and they disappear. As a result,

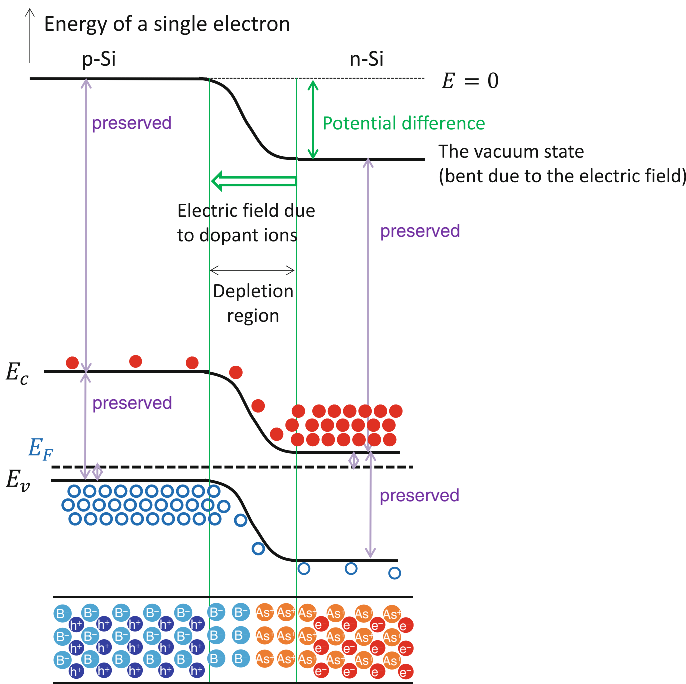

Fig. 3 The band lineup of a silicon pn junction. The *bottom cartoon* depicts the distribution of dopant ions (B^- and As^+) as well as electrons and holes. At the junction, depletion region is formed where electrons and holes are absent due to recombination and an electric field emerges as a result of negative and positive charges of dopant ions

the negative ions in the p-region and the positive ions in the n-region, which are immobile because they compose chemical bonds with the host silicon atoms, forms charge distribution and an electric field emerges. Since the energy of an electron, which is the vertical axis of the band diagram, is affected not only by the existence of neighboring atomic cores but also by such an electric field spreading over a large number of atomic cores, the energies of all the electron states (and the vacuum state as the origin of electrons' energy states) changes as a function of the position in the pn junction. This is a well-known band bending that emerges when different kinds of semiconductors (and metals) are put together. The band bending prevents electrons and holes from both migrating to the junction front and disappearing by recombination. As a result of these two competing processes at the junction front, the recombination of electrons and holes and the emergence of the electric field that prevents the additional supply of electrons and holes, establish equilibrium for the concentrations of electrons and holes.

Such equilibrium can be described in terms of thermodynamics. The criteria of thermodynamic equilibrium is the balance of free energy. It is therefore vital to obtain the free energies for electrons and holes. In general, free energy F for an ensemble of particles is described as

$$F = E - TS, \tag{2}$$

where E is internal energy, T is temperature and S is entropy. Conventional discussion on the behavior of electrons and holes employs energy per a particle, not for a mole of particles as is often employed in chemistry, and here we also discuss all the energies per a particle. Let us neglect the term associated with a work by volume expansion and use Helmholtz free energy (this is not exactly correct as we can see in the following section).

According to the Fermi-Dirac distribution of electrons, a majority of electrons and holes exist at the states with the energy close to the band edges. More precisely, the averaged energy of electrons in the conduction band is

$$E_{avr}(\text{electrons}) = E_c + \frac{3}{2}kT. \tag{3}$$

The detailed derivation is found in Sect. 9. The term $(3/2)kT$ can be regarded as the averaged kinetic energy of a particle moving in 3-dimensional space and this term is negligibly small compared with E_c since kT is approximately 1/40 eV at room temperature while E_c takes an order of eV. In this section, we will neglect the term $(3/2)kT$.

The entropy for an electron approximately takes the form

$$S = -k\ln\left(\frac{n}{N_c}\right). \tag{4}$$

This can be derived based on the definition of entropy in statistical mechanics:

$$S = \left(\frac{1}{n}\right) k \ln W, \tag{5}$$

where W is the number of possible arrangements for n electrons to occupy their places out of N_c sites, with n and N_c as numbers in a unit volume. The denominator n is for the purpose of obtaining entropy per a single electron.

To obtain Eq. (4) from Eq. (5), a well-known mathematical relationship is used

$$W = \frac{N_c!}{(N_c - n)!n!}, \tag{6}$$

with Stirling's approximation:

$$\ln x! \approx x \ln(x) - x. \tag{7}$$

In most cases, n is much smaller than N_c and an approximation $N_c - n \approx N_c$ is used.

The discussion above leads to the expression for the free energy of an electron:

$$E_{Fn} = E_c + kT \ln\left(\frac{n}{N_c}\right), \tag{8}$$

where the subscript n of E_{Fn} denotes electrons. Equation (8) actually is well known in solid state physics as Fermi level for electrons. This is not at all a coincidence but has a profound meaning; Fermi level is equivalent to free energy if we apply thermodynamics to the electrons in a semiconductor!

It is important to exaggerate the difference between internal energy and free energy. For an electron in a semiconductor, its internal energy is fixed at the edge of the conduction band E_c (if we neglect the contribution of kinetic energy $(3/2)kT$). On the other hand, the free energy of an electron can be altered by electron concentration n by adding dopant atoms for example. The larger electron concentration is, the closer its free energy approached to its internal energy by the reduction of entropy term TS. In other words, increasing electron concentration boosts the free energy through the reduction in entropy.

3 The Energy of Holes

It is important to recognize that the energy of a hole takes the opposite sign with respect to the energy of an electron that has been removed to make the hole. Let us consider two states with and without a hole as in Fig. 4. The energy of a hole is

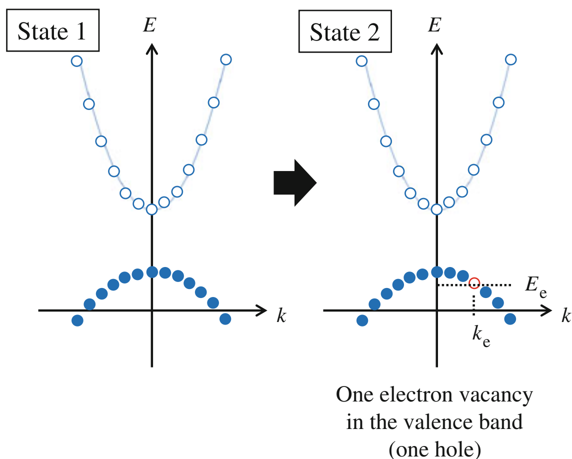

Fig. 4 Two states with and without a hole. In the state 2, an electron has been removed, leading to the appearance of a hole in the valance band

obtained by taking the difference in the total energy between the state 2 with a hole and the state 1 without a hole.

$$E_h = \sum_{state\,2} E - \sum_{state\,1} E. \tag{9}$$

The only difference between the two states is the absence of an electron in the state 2 and the total energy of the state 2 can be equalized to that of the state 1 by adding the energy of a missing electron E_e.

$$\sum_{state\,1} E = \sum_{state\,2} E + E_e. \tag{10}$$

From Eqs. (9) and (10), it is clear that the sign of energy is opposite between an electron and a hole:

$$E_h = -E_e. \tag{11}$$

This complexity stems from the concept of holes: a hole is not a real particle but a virtual one describing the vacancy of an electron. As a result, both the internal energy and the free energy of a hole should be accompanied by a negative sign, or these energies increases downwards in an energy diagram, when the energy of a hole is discussed simultaneously with that of an electron.

We can now discuss on the free energy of a hole in analogy to the one for an electron. The internal energy of a hole is approximately the energy of the valance band edge E_v. The entropy of a hole can be described using the hole concentration p and the effective density of states N_v in the valence band, which can be regarded as the maximum number of the states that holes can occupy:

$$S = -k\ln\left(\frac{p}{N_v}\right). \tag{12}$$

Then the free energy of a hole can be obtained as

$$-E_{Fp} = -E_v + kTln\left(\frac{p}{N_v}\right), \tag{13}$$

where the subscript p of E_{Fp} denotes holes. Both the free energy E_{Fp} and the internal energy E_{v} are accompanied by a negative sign because they are the energies for a hole. The entropy term, however, has the same sign as the formula for an electron (Eq. (8)) because the derivation of entropy depends solely on the combination of particles occupying the states, regardless of whether the particle is real or virtual.

Equation (13) can be converted to a famous form:

$$E_{Fp} = E_v - kTln\left(\frac{p}{N_v}\right), \tag{14}$$

which is identical to the expression of the Fermi level for holes. Fermi level is identical to free energy not only for electrons but also for holes. Interestingly, Eq. (14) can be derived from the formula of electron free energy (Eq. (8)) using the low of mass action (Eq. (1)) and the relationship

$$E_g = E_c - E_v. \tag{15}$$

This fact indicates that electron free energy and hole free energy take the same value, i.e., both particles are in equilibrium, when the law of mass action holds true.

4 Equilibrium of Electrons and Holes in a pn Junction

In a semiconductor under equilibrium, i.e., without an external work, electrons and holes take the same free energy and it changes according to doping as depicted in Fig. 2. When a junction of p- and n-type semiconductors is in equilibrium, thermodynamics imposes the equal free energy (or Fermi level) for the entire region of the structure. At the same time, apart from the junction front, i.e., outside the depletion region, the concentrations of electrons and holes never changes from the original value before forming the junction, and the free energy (or Fermi level) stays at the same position with respect to the band edges. These two requirements result in the band bending in the depletion region and the size of the band-edge offset is equal to the difference in the free energies in p- and n- regions. The exact shape of the band bending is determined by electrostatics: the distribution of charge density in the vicinity of the junction front, which emerges as a result of the depletion of electrons and holes, results in the band bending according to Poisson’s equation.

As depicted in Fig. 3, most of electrons exist in the n-region because of the slope of the band-edge energy E_c accelerates the electrons whose energy is close to E_c to the direction of the n-region. However, some of the electrons in the n-region have sufficient kinetic energy to climb up the slope of E_c and migrate to the p-region. From the n-region to the p-region, electron concentration n decreases exponentially as the band-edge energy E_c increases, following

$$n = N_c \exp\left(-\frac{E_c - E_F}{kT}\right), \tag{16}$$

which is the relationship transformed from Eq. (8), with the constant free energy E_{Fn}. Hole concentration similarly follows the relationship upon a change in E_v,

$$p = N_v \exp\left(-\frac{E_F - E_v}{kT}\right), \tag{17}$$

which is converted from Eq. (14).

5 Free Energies of Electrons and Holes in a Metal and a Schottky Junction

For metals, electrons occupy the quantum states to the middle of a band and there is no bandgap on the top of the states occupied by electrons. In this situation, according to Fermi-Dirac distribution, the concentrations of electrons and holes are so large that the entropy of electrons and holes is almost zero. Accordingly, the free energy of electrons corresponds to the energy top of the quantum states that electrons occupy at 0 K. (At a temperature higher than 0 K, some electrons are excited to higher-energy states than the energy top at 0 K). Above the electron free energy, a lot of unoccupied quantum state exist and they can exchange electrons with occupied states upon external force, leading to free motion of holes as well as electrons. Therefore, we can assume that a collection of holes exist at the energy states neighboring to electrons and the free energy of holes takes the same value as that of electrons in a metal. Note that the entropy of electrons and holes in a metal is almost zero and the free energy is independent of the concentration of electrons and holes, resulting in a constant value of the free energies for electrons and holes across the spatial axis.

We can now discuss the equilibrium for a junction between a metal and a semiconductor: a Schottky junction. Similarly to the case of a semiconductor pn junction, free energy is equalized for the entire structure and the position of the free energy with respect to the band edges is preserved for a semiconductor region apart from the junction (i.e., outside the depletion region). As depicted in Fig. 5, the free energy takes the same value across the entire structure. The band bending in a semiconductor emerges in order to equalize the free energies in a metal and that in a semiconductor,

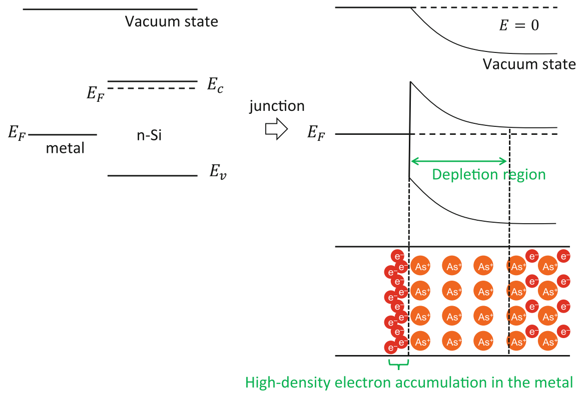

Fig. 5 The band lineup for a Schottky junction between a metal and an n-type semiconductor. The distribution of electrons, holes and ionized impurities is also shown at the *bottom schematic*

which had been different before forming the junction. The band bending is formed as a result of electron depletion in a part of semiconductor close to the junction, i.e., a depletion region. The electrons which initially existed there accumulates in the metal region close to the junction front. Nevertheless, the locally large concentration of electrons in the metal never affects the free energy in that region.

In reality, it often the case that a set of quantum states exist at the surface of a semiconductor because of the breakage of periodicity in atomic arrangement at the surface. These states often exist in the middle of the bandgap, which we call surface states or interfacial states. If electrons occupy these states, the free energy of electrons at the surface of a semiconductor is clamped to the energy of surface states because the density of such surface states is so small that the occupancy of states by electrons is large, making entropy almost zero. As a result, the electron free energy in a semiconductor aligns to the energy of surface states, which also determines the extent of band bending in the depletion region, as depicted in Fig. 6. Such a

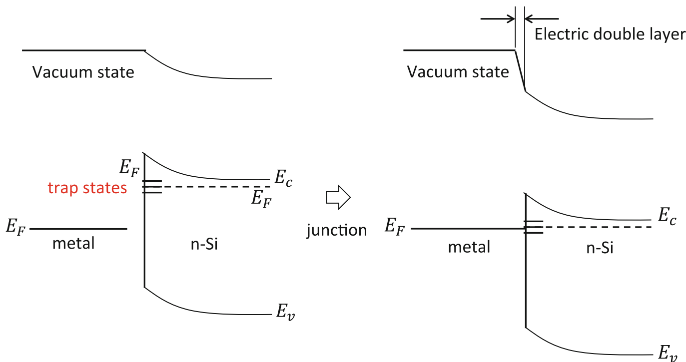

Fig. 6 The band lineup for a Schottky junction with trap states at the surface of a semiconductor

phenomena is often called as Fermi level pinning. When a semiconductor with such as surface state forms a junction with a metal, the band bending in a semiconductor is already determined by the energy of surface states and the misalignment of the electron free energy between the metal and the semiconductor is compensated by the appearance of the electric double layer at the metal/semiconductor interface. This is a very thin layer, less than a couple of nanometers, in which the opposite charges (electrons and holes) face each other between the metal and the semiconductor sandwiching the metal/semiconductor interface. The reason why we deal with such a complicated band alignment here is that the situation is quite similar to the interface between an electrolyte and a semiconductor which inevitably appears in photocatalysis and photoelectrochemistry using semiconductors.

6 Non-equilibrium in a Semiconductor

So far, we have discussed situations without external work applied to a semiconductor and the law of mass action has been always applicable. Here we will discuss situations in which some external work increases the concentrations of electrons and holes in a semiconductors from their equilibrium values.

The most readily-understandable situation may be the generation of electron-hole pairs in a semiconductor upon the absorption of photons. A photon absorbed in a semiconductor creates a pair of an electron and a hole by exciting an electron from a state in the valance band to another one in the conduction band. Such extra electrons and holes recombine and disappear as a successive event. The balance of the rates between generation and recombination determines the concentrations of electrons and holes upon light absorption by a semiconductor. Such concentrations of both electrons and holes are clearly larger than the values determined by the law of mass action (Eq. (1)). The electrons and holes in such a situation are no more in equilibrium. The increase in the concentration makes entropy smaller for both electrons and holes and the values defined by Eqs. (8) and (14) now take different values between electrons and holes. We call the value of E_{Fn} and E_{Fp} as quasi Fermi level for electrons and holes, respectively. Since electrons and holes are no longer in equilibrium, we have to define *quasi* free energies individually for electrons and holes.

The behavior of (quasi) free energies, or (quasi) Fermi levels, upon light absorption is depicted in Fig. 7. For an intrinsic semiconductor, light irradiation increases the concentrations of both electrons and holes by Δn and Δp, respectively, where $\Delta n = \Delta p$. Quasi Fermi levels approach to the band edge energies following Eqs. (8) and (14) upon an increase of electron and hole concentrations to $n + \Delta n$, $p + \Delta p$, respectively. Then a splitting $\Delta\mu$ ($= E_{\mathrm{Fn}} - E_{\mathrm{Fp}}$) emerges between the quasi free energies of electrons and holes. If we are able to take an electron and a hole out of the semiconductor under light irradiation while avoiding their recombination, the pair of an electron and a hole can generate external work if they can recombine at a place outside the semiconductor and release the difference of free energies $\Delta\mu$. The

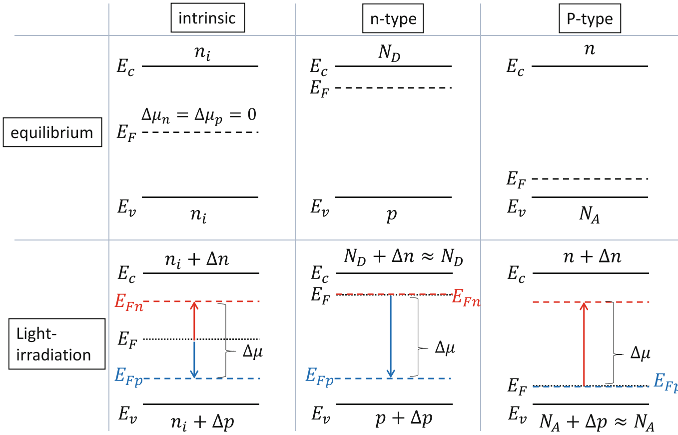

Fig. 7 The positions of Fermi levels and quasi Fermi levels for semiconductors in equilibrium and under light irradiation. For the latter (*bottom row*), the dotted lines denoted as E_F indicates the position of Fermi levels without light irradiation for reference. n and p denote electron and hole concentration, respectively, and N means the concentration of dopants with the subscripts D as donor and A as acceptor, respectively

splitting between the quasi Fermi levels for electrons and holes, $\Delta\mu$, is therefore very important as a measure of the maximum work if a pair of an electron and a hole is extracted out of a semiconductor.

For a n-type semiconductor without light irradiation, the electron concentration is determined by the dopant concentration N_D, and the hole concentration p is very small so that the product $N_D\,p$ satisfies the law of mass action. Upon light absorption, the electron and the hole concentrations increase by Δn and Δp, respectively. But Δn is much smaller than the initial electron concentration N_D and almost no change is brought about in the electron quasi Fermi level E_{Fn}. On the other hand, the hole concentration increases substantially from the initial value p, leading to a substantial shift of the hole quasi Fermi level E_{Fp} to the direction of valence-band-edge energy. For a p-type semiconductor, similarly, only the electron quasi Fermi level moves upon light absorption. In this manner, for a doped semiconductor, only the quasi Fermi level of minority carriers moves upon light absorption and the quasi Fermi level of majority (doped) carriers is almost never changed.

7 Semiconductor Device Structures for Energy Harvesting from Light

Based on the considerations on non-equilibrium of carriers in a semiconductor, let us look at a couple of structures including a semiconductor which serve for energy harvesting from light. The first example is a semiconductor photocatalyst. Figure 8 depicts its conceptual structure. Here, two metals with different Fermi levels are

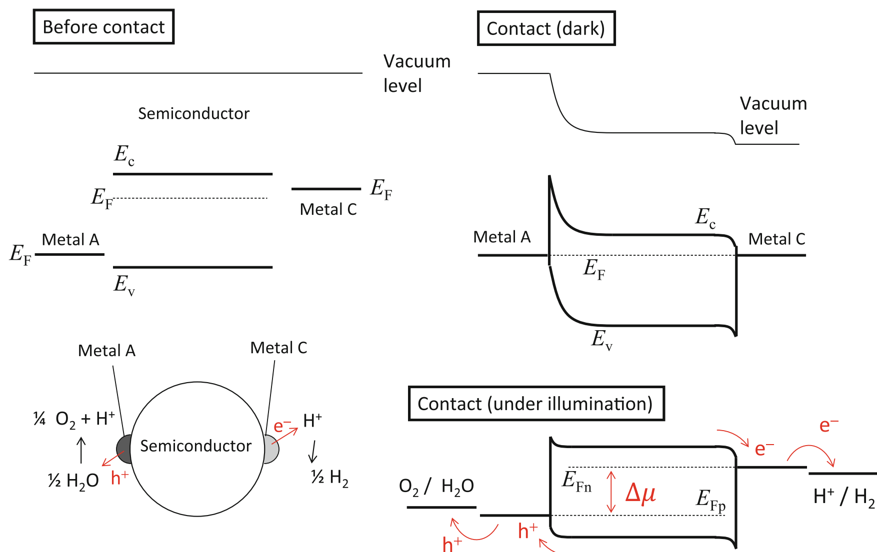

Fig. 8 The *left-bottom* schematic depicts an idealized semiconductor photocatalyst with two metals serving as selective contacts for electrons and holes. The metals also function as catalysts for the transfer of electrons and holes to the molecules in an electrolyte. Three diagrams depicts band lineup and (quasi) Fermi levels before making a contact, a contact under dark and illumination. For the band lineup under illumination, the vacuum level is omitted because its misalignment between an electrolyte and a semiconductor is not straightforward; it is affected by the electric double layer at the electrolyte/semiconductor interface and is strongly dependent on the surface. The level denotes as "H^+/H_2" is the redox potential for H_2 evolution from H^+, which is described in another chapter. Similarly, the level with the notation "O_2/H_2O" is the redox potential for O_2 evolution from H_2O

attached to a semiconductor particle which is slightly doped to be n-type. Theoretically, an intrinsic semiconductor can serve for energy harvesting from light. In reality, however, it is often difficult to obtain a genuinely intrinsic semiconductor with extremely high purity. In addition, slight doping helps deactivate crystal defects as centers for electron-hole recombination without photon emission, i.e., a process leading to energy dissipation, by filling the quantum energy states in the band gap associated with crystal defects. It is therefore realistic to apply a slight doping to a bulk of semiconductor. Figure 8 supposes such a situation in which an entire semiconductor particle is doped to be slightly n-type.

Under a dark condition, the Fermi level in the metal C is aligned to the Fermi level of the semiconductor so that the slope of E_c in the vicinity of the junction favors the transport of electron to the metal C while hole transport to the metal C is conversely blocked by the slope of E_v. The mismatch of Fermi level between the metal A and the semiconductor forms a large band bending, which blocks (favors) the transport of electrons (holes) to the metal A. Note that no net transport of carriers exist in the junction under equilibrium and the discussion on the ease of transport here is only for the carriers that exist in excess of the equilibrium

concentration upon external work such as light illumination. Since the semiconductor here is n-type, almost no holes exist and we normally focus on the transport of electrons. This is why we call the junction with the metal C as "ohmic" (conductive) and the junction with the metal A as Schottky (rectifying or inslative under a zero bias condition).

Upon illumination, the generation of extra electrons and holes in the semiconductor splits the quasi Fermi levels for electrons and holes. The remaining band bending still favors the transport of electrons to the metal C and that of holes to the metal A. As a result, an electron-hole pair with the difference of free energy $\Delta\mu$ is split to the different directions, making it possible to extract work $\Delta\mu$ out of the semiconductor.

Now, the electrons in the metal C and the holes in the metal A have the free energies, i.e., quasi Fermi levels: E_{Fn} for the electrons and E_{Fp} for the holes, respectively. These values are determined by the band-edge energies of the semiconductor bulk and the concentrations of electrons and holes that exist in the semiconductor based on Eqs. (8) and (14). On the other hand, there exists a relationship between the band-edge energies of semiconductors and the standard electrode potentials for a variety of redox reactions in an electrolyte, as is described in the previous chapter. If, as is the situation in Fig. 8, the free energy of the electrons in the metal C, E_{Fn}, exists at the upper side of a redox reaction, electrons can be transferred from the metal C to the molecules in an electrolyte participating in the reaction. Note that this is a consideration in terms of thermodynamics and just the possibility of the reaction progress is predicted; nothing is known about the rate of the electron transfer. Similarly, if the free energy of the holes in the metal A, E_{Fp}, exists at the lower side of a redox reaction, holes can be transferred from the metal A to the molecules in an electrolyte participating in the reaction. It should be kept in mind that the energy of holes increases downwards in an energy diagram that depicts the energy of an electron. This is an ideal operation mode of a semiconductor photocatalyst in an electrolyte; a semiconductor particle with the surface modified by two appropriate kinds of metals can serve for water splitting upon light irradiation.

Of course, if we expand the size of the hypothetical structure in Fig. 8 and connect two electrical wires to the metals A and C, we can extract electrons and holes to an external device with the difference in the free energies $\Delta\mu$ between electron and holes. This is a photovoltaic cell using one Schottky junction (at the interface with the metal A) and the other junction that favors the transfer of the majority carriers in the semiconductor (in this case, electron) at the semiconductor/metal interface, which is often called ohmic junction.

As for a photovoltaic cell, it is more common to use a semiconductor pn junction for the purpose of separating electrons and holes to different electrodes. A typical solar cell employs a pn junction in the vicinity of a surface as depicted in Fig. 9. In this example, a thicker region is n-type but it can be p-type with an n-region at the surface. The back side is contacted to the metal C with ohmic band alignment by employing a metal with its original Fermi level a bit larger than the Fermi level of the n-type semiconductor, similarly to the case in Fig. 8. As for the metal contacting

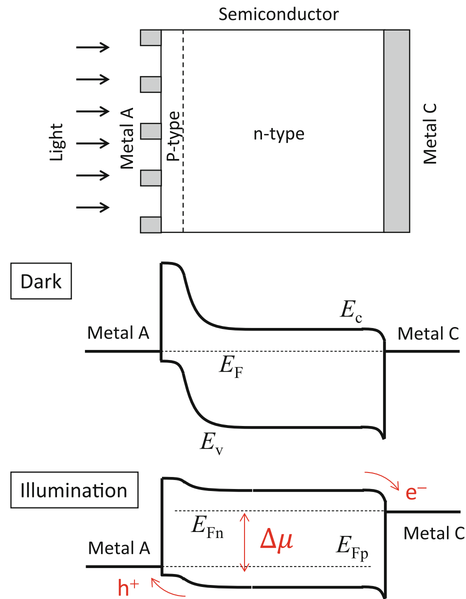

Fig. 9 *Upper schematic* depicts a typical photovoltaic cell using a semiconductor pn junction with two metals serving as contacts for electrons and holes, respectively. Bottom two diagrams depict the band lineup and (quasi) Fermi levels under dark and illumination

to the p-region of the semiconductor, the metal A is assumed to have the same Fermi level as the one in the semiconductor p-region for the simplicity of the picture. The resultant slope of the conduction-band-edge energy, E_c, favors the majority of electrons with smaller kinetic energies to migrate to the direction of the metal C. Since the electrons are in equilibrium across the device structure, a small fraction of electrons exist in the vicinity of the metal A, where E_c is much larger, but the majority exist in the n-region and the metal C. Similarly, the majority of holes prefers moving to the direction of the metal A owing to the slope of E_v.

Under illumination, similar to the case of a photocatalyst in Fig. 8, the quasi Fermi levels are split and band bending becomes smaller, but still a slope of E_c and E_v exist and it separates electrons and holes to different directions. The electrons in the metal C and the hole in the metal A have different free energies and they can make external work if they are led to an external device.

If we compare the situations in Figs. 8 and 9, it is clear that a Schottky junction and a pn junction work in a similar manner to separate electrons and holes. The maximum difference in free energy (or quasi Fermi levels) $\Delta\mu$ is obtained when intensive light absorption generates abundant electrons and holes accumulated in the conduction and the valence bands, respectively. In this situation, a large electron (hole) concentration makes it difficult for the positive donor (negative acceptor) ions in a crystal lattice to exist unaccompanied by electrons (holes), where naked ions are the source of a depletion region as depicted in Figs. 3 and 5. Such difficulty of making a depletion region makes the bands flat upon the existence of abundant electrons and holes in a semiconductor. This favors large $\Delta\mu$ as is understandable by the band-lineup charts in Figs. 8 and 9. Such a flat-band situation, however, lacks

electric field inside, making it difficult to drive electrons and holes to the separated electrodes. This is called "open-circuit" situation when we can obtain the maximum $\Delta\mu$ (or voltage in the case of a photovoltaic cell) while no current is obtained.

One practical disadvantage of Schottky junction is that it is not easy to make a large band bending in the semiconductor. Even though an appropriate metal is employed which have a sufficiently large difference in Fermi level with respect to the one in a semiconductor, the existence of semiconductor surface states prevents a large band bending as expected from the difference in Fermi levels. On the other hand, it is relatively easy to have a large band bending at a pn junction and this is why a pn junction is a common structure in photovoltaic devices for the separation of electrons and holes.

8 Fermi-Dirac Distribution of Electrons in the Bands and Effective Density of States

This section can be skipped if the reader is not so familiar with solid-state physics. More detailed discussion is found in many textbooks on semiconductor physics such Refs. [1] and [2].

Here we will review a conventional theory on how electrons populate in the conduction and the valence bands and we will find a connection to the thermodynamic treatment of the concentrations of electrons and holes in a semiconductor. An ordinary discussion of electron occupancy of the quantum states in a semiconductors first assumes Fermi level, E_F. As depicted in Fig. 10, the electron density in each energy segment $n(E)$ is determined by the product between the density of states in the conduction band $D_e(E)$ and the probability of an electron occupying a state at energy E, $f(E)$.

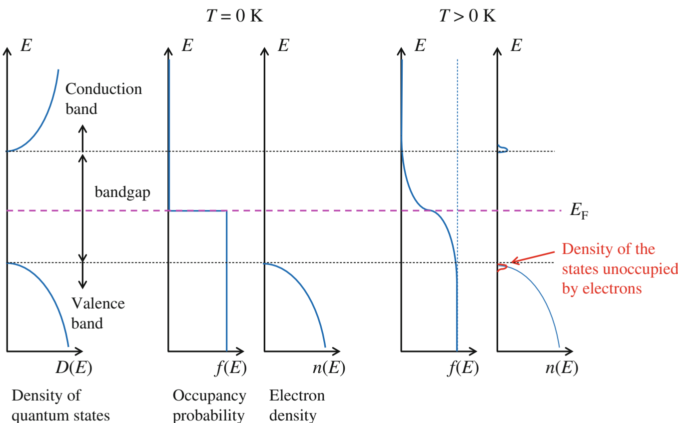

Fig. 10 Distribution of electrons along its energy in the bands of a semiconductor

$$n(E) = D_e(E)f(E), \tag{18}$$

where

$$D_e(E) = 4\pi\left(\frac{2m_e^*}{h^2}\right)^{\frac{3}{2}}(E - E_c)^{\frac{1}{2}}, \tag{19}$$

i.e., the density of states increases according to the square root of the energy distance from the edge of the conduction band, where m_e^* is the effective mass of an electron in the conduction band and h is the Planck constant. $f(E)$ takes a well-known form of Fermi-Dirac distribution with a reference energy E_F, which we call Fermi level.

$$f(E) = \frac{1}{\exp\left(\frac{E-E_F}{kT}\right) + 1}. \tag{20}$$

With E_F positioned at a certain energy in the bandgap, at 0 K, electrons occupy the valence band completely and the conduction band is completely empty. At a temperature above 0 K, the function $f(E)$ makes a small portion of the states in the conduction band occupied by electrons and some of the states in the valence band become empty, which states are regarded as holes.

The total electron concentration is obtained by integrating $n(E)$ along the energy over the conduction band.

$$n = \int_{E_c}^{\infty} D_e(E)\exp\left(-\frac{E - E_F}{kT}\right)dE = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{\frac{3}{2}}\exp\left(-\frac{E_c - E_F}{kT}\right), \tag{21}$$

where $f(E)$ is approximated since $E - E_F \gg kT$:

$$f(E) \approx \exp\left(-\frac{E - E_F}{kT}\right), \tag{22}$$

meaning that Fermi-Dirac distribution is approximated as Boltzmann distribution if the energy of our interest is far enough from E_F. Equation (21) can be summarized as

$$n = N_c \exp\left(-\frac{E_c - E_F}{kT}\right), \tag{23}$$

with

$$N_c = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{\frac{3}{2}}. \tag{24}$$

The intuitive interpretation of Eq. (23) is that all the electrons take the energy of E_C and the density of quantum states N_C are concentrated at the same energy. The exponential term is the probability of electrons occupying the quantum states at the energy E_C with the origin of energy taken at E_F.

Interestingly, Eq. (23) is completely the same as Eq. (16) that was converted from Eq. (8), indicating that the Fermi level for electrons distribution along the energy axis is in essence the free energy of electrons according to a thermodynamic interpretation.

In a similar manner, the concentration of holes is obtained as:

$$p = N_v \exp\left(-\frac{E_F - E_v}{kT}\right). \tag{25}$$

where N_v is the effective density of states for holes. This is equivalent to the thermodynamic expression, Eq. (14). Multiplying the concentrations of electrons n and holes p with Eqs. (23) and (25) yields the law of mass action in Eq. (1). Here the relation in Eq. (15) is used. The discussion above clarifies that the thermodynamic treatment of carrier concentrations in a semiconductor is another viewpoint of Fermi-Dirac distribution of electrons in a semiconductor.

9 Detailed Derivation of Electron/Hole Free Energies in a Semiconductor

This section can be skipped if the reader is not so familiar with solid-state physics. The detailed discussion is in Ref. [3].

Let us first obtain the averaged energy of the electrons in the conduction band.

$$\langle \epsilon_e \rangle = \frac{1}{n_e} \int_{E_c}^{\infty} E D_e(E) f(E) dE = E_c + \frac{3}{2} kT. \tag{26}$$

Similarly, the averaged energy of the holes in the valence band is:

$$-\langle \epsilon_h \rangle = \frac{1}{n_h} \int_{E_v}^{-\infty} (-E) D_h(E) f(E) dE = -E_v + \frac{3}{2} kT, \tag{27}$$

where $D_h(E)$ is the density of states in the valence band, which takes the form of Eq. (19) with a substitution of m_e with m_h, effective mass of a hole in the valence band.

Here, the tedious process of calculation is omitted but we certainly get the relationship in Eq. (3). Because the kinetic energy of electrons and holes in 3-dimensional space is $(3/2)kT$, electrons and holes in a semiconductor can be regarded as monoatomic ideal gases. Then, we can apply the precise formulation of

entropy for a monoatomic ideal gas due to 3-dimensional translational motion, which is known as Sackur-Tetrode equation [4]:

$$S = k\left\{\frac{5}{2} + \ln\left(\left(\frac{2\pi m_e^* kT}{h^2}\right)^{\frac{3}{2}}\frac{1}{n}\right)\right\}, \tag{28}$$

where n is the electron concentration. Here we describe the derivation for the electrons but similar treatment is possible for holes. Using Eq. (24), we can obtain the expression

$$TS = kT\ln\left(\frac{N_c}{n}\right) + \frac{5}{2}kT. \tag{29}$$

Therefore, admitting that ϵ_e corresponds to the internal energy of an electron U, Gibbs free energy of an electron is

$$\begin{aligned} G = U + PV - TS = \langle\epsilon_e\rangle + PV - TS = \left(E_c + \frac{3}{2}kT\right) + kT - \left(kT\ln\left(\frac{N_c}{n}\right) + \frac{5}{2}kT\right) \\ = E_c + kT\ln\left(\frac{n}{N_c}\right) = E_{Fn}. \end{aligned} \tag{30}$$

Here, ideal gas equation $PV = kT$ is used and the last equator corresponds to Eq. (8). Now we can confirm that the Fermi level for the electrons in a semiconductor is equivalent to the Gibbs free energy for an electron in the viewpoint of thermodynamics. Similar derivation confirms that the Fermi level for holes is equivalent to the Gibbs free energy of a hole.

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