Photovoltage analysis of a heterojunction solar cell

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According to the p–n junction model of Shockley, the relationship between the equilibrium carrier concentrations of n-type and p-type semiconductors on the edges of the depletion region of a p–n junction solar cell is analysed. The calculation results show that the photovoltage can exceed the built-in voltage for a special kind of heterojunction solar cell. When the photovoltage exceeds the built-in voltage under illumination, the dark current and the photocurrent are impeded by the peak of voltage barrier at the interface and the expression of the total I–V characteristic is given.

Keywords: solar cells, built-in voltage, photovoltage, heterojunction

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1. Introduction

Attempts have been made to decrease the cost of solar cells by developing heterojunction solar cells and the efficiency of conversion for solar photons into electronic energy has been greatly improved in recent years.[1−6] It is well known that the maximum open circuit voltage of the p–n homojunction solar cell is the built-in potential of the junction and the maximum built-in potential is close to the energy gap.[7] For the heterojunction solar cell, the maximum built-in potential is influenced by the conduction-band and valence-band offset,[8−10] and the relationship between the maximum open circuit voltage and the built-in potential of the junction is fuzzy. In the present article, the relationship between the maximum open circuit voltage and the built-in potential of the junction is discussed and the expression of total I–V characteristic for heterojunction solar cell under illumination is given.

2. Theoretical analysis

A p–n junction solar cell consists of an n-type semiconductor and a p-type semiconductor. In thermal equilibrium, the diffusion current and the drift current for each carrier type are exactly balanced, so there is no net current flow. Assuming that the p-type region and the n-type region are sufficiently thick, the regions on either side of the depletion region are essentially charge-neutral (often termed quasi-neutral).[11] The electrostatic potential difference resulting from the junction formation is called the built-in voltage, $V_{\rm bi}$. It arises from the electric field created by the exposure of the positive and the negative space charge in the depletion region.

Figure 1 shows the energy-band diagram of a p–n heterojunction solar cell in thermal equilibrium. The two semiconductors are assumed to have different values of bandgap $E_{\rm g}$ (of which the smaller bandgap is of p-type, $E_{\rm gp} \leq E_{\rm gn}$) and different values of electron affinity χ (of which the smaller affinity is of p-type, $\chi_{\rm p} \leq \chi_{\rm n}$). The conduction-band offset is represented by $\Delta E_{\rm C}$ and the valence-band offset is denoted by $\Delta E_{\rm V}$.

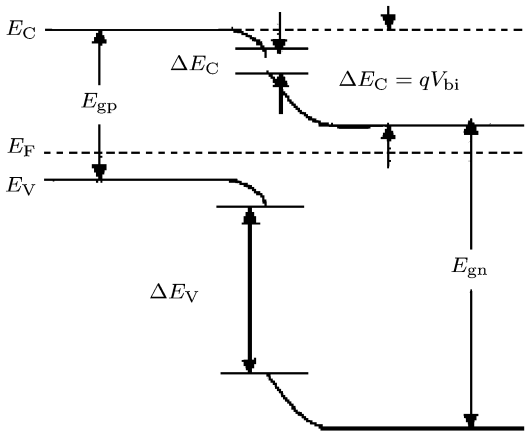


Fig. 1. Energy band structure diagram for a p–n heterojunction solar cell at thermal equilibrium under no illumination. The band gap for p-type semiconductor is smaller.

Under equilibrium conditions, zero applied voltage and no illumination, the Fermi energy, $E_{\rm F}$, is constant with respect to position. According to the law

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of the Shockley's p–n junction,[12−14] the relationship between the equilibrium carrier concentrations for n-type and p-type semiconductors on the edges of the depletion region can be expressed as

$$n_{\rm p0} = n_{\rm n0} \exp\left(-\frac{qV_{\rm bi} + \Delta E_{\rm C}}{k_0 T}\right), \quad (1)$$

$$p_{\rm p0} = p_{\rm n0} \exp\left(\frac{qV_{\rm bi} + \Delta E_{\rm V}}{k_0 T}\right), \quad (2)$$

where q is the electron charge quantity; k_0 is the Boltzmann's constant; T is the ambient temperature, the subscripts 'n' and 'p' refer to the types of semiconductors; the subscript '0' denotes the thermal equilibrium condition; $n_{\rm n0}$, $n_{\rm p0}$, $p_{\rm n0}$ and $p_{\rm p0}$ are the equilibrium concentrations of electrons and holes for n-type and p-type semiconductors, respectively.

Under illumination, the equilibrium is broken and a lot of carriers are induced by illumination in n-type and p-type semiconductors. The diffusion current is greater than the drift current for each type of carrier, so there is a net charge flow. The region on each side of the depletion region is not electrically neutral (often termed quasi-neutral). As a result, a photovoltage (V) is produced and the kinetic equilibrium is formed. Assuming that the illumination intensity is not enough to induce the photovoltage on the verge of the built-in voltage, according to the law of the Shockley's p–n junction, the relationship between the carrier concentrations for n-type and p-type semiconductors on the edge of the depletion region can be expressed as

$$\begin{aligned} & n_{\rm p0} + \Delta n_{\rm p} \\ = {} & (n_{\rm n0} + \Delta n_{\rm n}) \exp\left(-\frac{qV_{\rm bi} + \Delta E_{\rm C} - qV}{k_0 T}\right), \quad (3) \\ & p_{\rm n0} + \Delta p_{\rm n} \\ = {} & (p_{\rm p0} + \Delta p_{\rm p}) \exp\left(-\frac{qV_{\rm bi} + \Delta E_{\rm V} - qV}{k_0 T}\right), \quad (4) \end{aligned}$$

where $\Delta n_{\rm n}$, $\Delta n_{\rm p}$, $\Delta p_{\rm n}$ and $\Delta p_{\rm p}$ are the photo-induced electron and hole concentration for n-type and p-type semiconductors in the kinetic equilibrium, respectively.

When the illumination intensity is enhanced and the photovoltage equals the built-in voltage, Eqs. (3) and (4) are given as

$$n_{\rm p0} + \Delta n_{\rm p} = (n_{\rm n0} + \Delta n_{\rm n}) \exp\left(-\frac{\Delta E_{\rm C}}{k_0 T}\right), \quad (5)$$

$$p_{\rm n0} + \Delta p_{\rm n} = (p_{\rm p0} + \Delta p_{\rm p}) \exp\left(-\frac{\Delta E_{\rm V}}{k_0 T}\right). \quad (6)$$

If the illumination intensity is further strengthened, the photo-induced carrier concentrations will be increased in the n-type and p-type semiconductors. Assuming that the photovoltage cannot exceed the built-in voltage, Eqs. (5) and (6) can be expressed as

$$\begin{aligned} & n_{\rm p0} + \Delta n_{\rm p} + \delta n_{\rm p} \\ = {} & (n_{\rm n0} + \Delta n_{\rm n} + \delta n_{\rm n}) \exp\left(-\frac{\Delta E_{\rm C}}{k_0 T}\right), \quad (7) \\ & p_{\rm n0} + \Delta p_{\rm n} + \delta p_{\rm n} \\ = {} & (p_{\rm p0} + \Delta p_{\rm p} + \delta p_{\rm p}) \exp\left(-\frac{\Delta E_{\rm V}}{k_0 T}\right), \quad (8) \end{aligned}$$

where $\delta n_{\rm n}$, $\delta n_{\rm p}$, $\delta p_{\rm n}$ and $\delta p_{\rm p}$ are the increased photo-induced electron and hole concentrations for n-type and p-type semiconductors, respectively.

According to Eqs. (5)–(8), we can have

$$\delta n_{\rm p} = \delta n_{\rm n} \exp\left(-\frac{\Delta E_{\rm C}}{k_0 T}\right), \quad (9)$$

$$\delta p_{\rm n} = \delta p_{\rm p} \exp\left(-\frac{\Delta E_{\rm V}}{k_0 T}\right). \quad (10)$$

According to the electroneutrality principle, the number of increased photo-induced electrons should be equal to the number of increased photo-induced holes for a solar cell. So we can have

$$\delta n_{\rm p} L_{\rm p} + \delta n_{\rm n} L_{\rm n} = \delta p_{\rm n} L_{\rm n} + \delta p_{\rm p} L_{\rm p}, \quad (11)$$

where $L_{\rm n}$ and $L_{\rm p}$ are the effective thicknesses for n-type and p-type semiconductors. According to Eqs. (9)–(11), we obtain

$$\begin{aligned} & \delta n_{\rm n} \left[\exp\left(-\frac{\Delta E_{\rm C}}{k_0 T}\right) L_{\rm p} + L_{\rm n}\right] \\ = {} & \delta p_{\rm p} \left[\exp\left(-\frac{\Delta E_{\rm V}}{k_0 T}\right) L_{\rm n} + L_{\rm p}\right]. \quad (12) \end{aligned}$$

For an n-type semiconductor, the net increased photo-induced electron concentration can be expressed as

$$\begin{aligned} \Delta(\delta n) = {} & \delta n_{\rm n} - \delta p_{\rm n} \\ = {} & \delta n_{\rm n} \left[\frac{1 - \exp\left(-\dfrac{\Delta E_{\rm C} + \Delta E_{\rm V}}{k_0 T}\right)}{\exp\left(-\dfrac{\Delta E_{\rm V}}{k_0 T}\right) \dfrac{L_{\rm n}}{L_{\rm p}} + 1}\right] > 0. \quad (13) \end{aligned}$$

For a p-type semiconductor, the net increased photo-induced hole concentration can be written as

$$\begin{aligned} \Delta(\delta p) = {} & \delta p_{\rm p} - \delta n_{\rm p} \\ = {} & \delta p_{\rm p} \left[\frac{1 - \exp\left(-\dfrac{\Delta E_{\rm V} + \Delta E_{\rm C}}{k_0 T}\right)}{\exp\left(-\dfrac{\Delta E_{\rm C}}{k_0 T}\right) \dfrac{L_{\rm p}}{L_{\rm n}} + 1}\right] > 0. \quad (14) \end{aligned}$$

According to Eqs. (13) and (14), we can know that there exist net increased photo-induced electrons or holes for the n-type and the p-type semiconductors. As a result, an electric field should be induced by the net increased carriers between the n-type and p-type semiconductors. The hypothesis that the photovoltage cannot exceed the built-in voltage ($V \leq V_{\rm bi}$) is a false assumption for the heterojunction solar cells. So we can conclude that the further enhancement of illumination intensity can increase the photovoltage and the photovoltage can exceed the built-in voltage for the heterojunction solar cells.

For the homojunction solar cell, $\Delta E_{\rm C} = 0$ and $\Delta E_{\rm V} = 0$. According to Eqs. (9)–(11), we have

$$\delta n_{\rm p} = \delta n_{\rm n} = \delta p_{\rm n} = \delta p_{\rm p}. \tag{15}$$

For an n-type semiconductor, the net increased photo-induced electron concentration can be expressed as

$$\Delta(\delta n) = \delta n_{\rm n} - \delta p_{\rm n} = 0. \tag{16}$$

For a p-type semiconductors, the net increased photo-induced hole concentration can be written as

$$\Delta(\delta p) = \delta p_{\rm p} - \delta n_{\rm p} = 0. \tag{17}$$

According to Eqs. (16) and (17), we can know that there occurs no net increased photo-induced electron or hole for the n-type and p-type semiconductors, respectively. So the photovoltage cannot be increased by the further enhancement of illumination intensity and the maximal photovoltage equals the built-in voltage for the homojunction solar cell.

3. Results and discussion

According to the above analysis, we can conclude that the maximal photovoltage cannot exceed the built-in voltage for the homojunction solar cell and the photovoltage can exceed the built-in voltage for the heterojunction solar cell. When the photovoltage exceeds the built-in voltage for the heterojunction solar cell, the major carriers transform from the exhausted state to accumulation at the interface of the p–n heterojunction. The energy-band diagrams can be shown in Fig. 2. At the interface of the p–n heterojunction, the conduction band and valence band bent in the opposite directions.

As shown in Fig. 2, the photovoltage V is equal to

$$V = V_{\rm bi} + V_{\rm a1} + V_{\rm a2}. \tag{18}$$

Because $V_{\rm a1}$ and $V_{\rm a2}$ are induced by the major carrier accumulation, the thicknesses of the major carrier accumulation in the n-type and the p-type semiconductors should be equal. As a result, $V_{\rm a1}$ is equal to $V_{\rm a2}$ and

$$V_{\rm a1} = V_{\rm a2} = \frac{V - V_{\rm bi}}{2}. \tag{19}$$

The total I–V characteristic of solar cell under illumination can be simply a sum of the dark current and the photocurrent, given as[7]

$$I = I_{\rm s}\left[\exp\left(\frac{qV}{k_0T}\right) - 1\right] - I_{\rm L}, \tag{20}$$

where $I_{\rm s}$ is the diode saturation current, $I_{\rm s}\left[\exp\left(qV/k_0T\right) - 1\right]$ is the dark current, $I_{\rm L}$ is the photocurrent and results from the excitation of excess carriers by solar radiation.

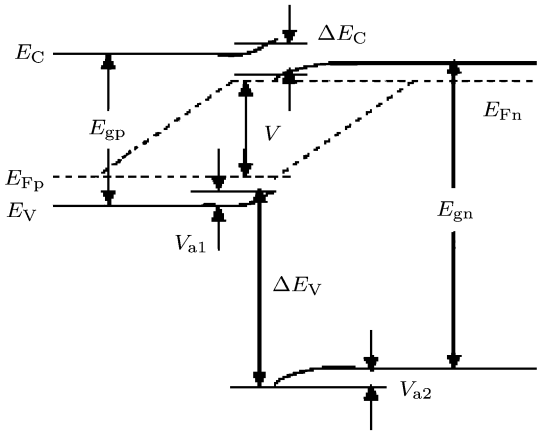


Fig. 2. Energy band structure diagram for a p–n heterojunction solar cell under illumination, with the photovoltage exceeding the built-in voltage.

For the heterojunction solar cell, when the photovoltage exceeds the built-in voltage under illumination, the dark current and the photocurrent should be impeded by the peak of voltage barrier at the interface. The photocurrent can be expressed as

$$I_{\rm L}\exp\left(-V_{\rm a1}\right) = I_{\rm L}\exp\left(-\frac{V - V_{\rm bi}}{2k_0T}\right). \tag{21}$$

The dark current can be expressed as

$$\begin{aligned} &I_{\rm s}\left[\exp\left(\frac{qV}{k_0T}\right) - 1\right]\exp[-\left(V - V_{\rm a2} - V_{\rm bi}\right)] \\ &= I_{\rm s}\left[\exp\left(\frac{qV}{k_0T}\right) - 1\right]\exp\left(-\frac{V - V_{\rm bi}}{2k_0T}\right). \end{aligned} \tag{22}$$

So the total I–V characteristic of heterojunction solar cell under illumination is as follows:

when the photovoltage does not exceed the built-in voltage ($V \leq V_{\rm bi}$),

$$I = I_{\rm s}\left[\exp\left(\frac{qV}{k_0T}\right) - 1\right] - I_{\rm L}; \tag{23}$$

when the photovoltage exceeds the built-in voltage ($V \geq V_{\rm bi}$),

$$I = \left\{I_{\rm s}\left[\exp\left(\frac{qV}{k_0T}\right) - 1\right] - I_{\rm L}\right\} \times \exp\left(-\frac{V - V_{\rm bi}}{2k_0T}\right). \tag{24}$$

4. Conclusion

According to the law of Shockley's p–n junction, the relationship between the equilibrium carrier concentrations for n-type and p-type semiconductors on the edge of the depletion region for the p–n junction solar cell is analysed. Calculation results show that the photovoltage can not be greater than the built-in voltage and the maximal photovoltage equals the built-in voltage for the homojunction solar cell; the photovoltage can exceed the built-in voltage for the heterojunction solar cell. For the heterojunction solar cell, when the photovoltage exceeds the built-in voltage under illumination, the dark current and the photocurrent should be impeded by the peak of voltage barrier at the interface and the total I–V characteristic can be expressed as Eq. (24). Using heterojunction structure may improve photoelectric conversion efficiency of solar cells, especially in light-gathering solar cells.

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