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## THE SOURCES OF PHOTOVOLTAGE IN SOLAR CELLS

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A general expression for the open circuit voltage in solar cells employing inhomogeneous semiconductors is derived. The analysis is based on the exact solution of the Boltzmann transport equation in relaxation time approximation. It assumes the cubic symmetry and an ellipsoidal band structure for the conduction and valence bands. It is found that the photovoltage arises from the built-in electric field and the gradients of the average kinetic energy densities, effective masses and the affinities of electrons and holes. By considering a plausible form for the average kinetic energies of an electron and a hole, it is shown that in addition to already known sources of the photovoltage, obtained from the first order solution of the Boltzmann transport equation, the photovoltage can also arise from the gradients of equilibrium concentration and mobilities of electrons and holes and the photoelectric field.

## I - INTRODUCTION

Over the course of the development of solar cells employing the semiconductor materials, several sources of the photovoltage have been identified. According to some earlier investigations<sup>1</sup> the photovoltage in solar cells was proposed to arise due to the pressure exerted by photons on the electrons in the solar cell material. Subsequent investigations show that the principal origin of the photovoltage is the separation of charged carriers (electrons and holes) in the depletion region which provides a built-in electric field. Later on a systematic analysis<sup>2,3</sup> of the origin of the photovoltage sources in inhomogeneous semiconductors showed that in addition to the built-in electric field, photovoltage could originate from Dember effect due to the difference in the relative concentration gradients of electrons and holes and the gradients of affinities and effective masses of electrons and holes. This analysis is based on the first order solution of the Boltzmann transport equation (BTE) in relaxation time approximation. In transport regions of high electric field, first order solution of the BTE cannot be considered a good approximation<sup>4</sup>. Various analytical and numerical methods<sup>4</sup>, based on some approximations, have been developed to go beyond first order solution of the BTE. The aim of this paper is to analyse the sources of the photovoltage from the exact solution of the BTE.

In Section II we have obtained the generalized expressions for the electron and hole current densities in inhomogeneous semiconductors with position dependent band structures. In Section III these generalized expressions for the current densities are used to obtain the open circuit voltage and the various sources of the photovoltage are identified. A brief summary of the principal results is given in Section IV.

## II - GENERALIZED ELECTRON AND HOLE CURRENT DENSITIES

When the light falls on a solar cell employing semiconductor materials, electrons in the conduction band and holes in the valence band are created. Due to built-in electric field, these electrons and holes flow in opposite directions and thus produce electrons and hole currents in the solar cell. From a macroscopic point of view the electron and hole current densities are usually assumed to originate from drift and diffusion

processes. But for a proper understanding of the processes involved, they should be derived from the BTE. For electrons in the conduction band or holes in the valence band, the BTE in relaxation time approximation for inhomogeneous semiconductors with position dependent band structure can be written as<sup>5</sup>

$$\begin{aligned} \frac{\partial f_s(\mathbf{k}, \mathbf{r}, t)}{\partial t} + \frac{1}{\hbar} [\nabla_{\mathbf{k}} \epsilon_s(\mathbf{k}, \mathbf{r}) \cdot \nabla f_s(\mathbf{k}, \mathbf{r}, t) - \nabla \epsilon_s(\mathbf{k}, \mathbf{r}) \cdot \nabla_{\mathbf{k}} f_s(\mathbf{k}, \mathbf{r}, t)] \\ = - \frac{f_s(\mathbf{k}, \mathbf{r}, t) - f_s^0(\mathbf{k}, \mathbf{r})}{\tau_s(\mathbf{r})} \end{aligned} \quad (2.1)$$

where,  $s = \pm$ ,  $s = +$  corresponds to holes in the valence band and  $s = -$  corresponds to electrons in the conduction band,  $\hbar$  is the planck's constant divided by  $2\pi$ ,  $f_s(\mathbf{k}, \mathbf{r}, t)$  is the local nonequilibrium electron or hole distribution function for the wave-vector  $\mathbf{k}$  and position  $\mathbf{r}$  at the time  $t$ ,  $f_s^0(\mathbf{k}, \mathbf{r})$  is the corresponding local equilibrium distribution function,  $\epsilon_s(\mathbf{k}, \mathbf{r})$  is the position dependent band energy of an electron or a hole, and  $\tau_s(\mathbf{r})$  is the electron or hole relaxation time due to scattering. For simplicity the relaxation time which depends upon both wave-vector and position, is assumed to be independent of the wave-vector. Although it is strictly true only for scattering due to neutral impurities, it can be thought of as a local average relaxation time which may depend on the average kinetic energy of electrons or holes and the applied forces.

In semiclassical approximation the band energy  $\epsilon_s(\mathbf{k}, \mathbf{r})$  can be expressed as

$$\epsilon_s(\mathbf{k}, \mathbf{r}) = E_s(\mathbf{r}) - sW_s(\mathbf{k}, \mathbf{r}) \quad (2.2)$$

where,  $E_s(\mathbf{r})$  is the energy of the conduction band minima for  $s = -$  and the energy of the valence band maxima for  $s = +$ , and  $W_s(\mathbf{k}, \mathbf{r})$  is the kinetic energy of an electron or a hole. For the semiconductors used in solar cells we can assume  $W_s(\mathbf{k}, \mathbf{r})$  reasonably well by an ellipsoidal band structure

$$W_s(\mathbf{k}, \mathbf{r}) = \sum_{i=x,y,z} W_{is}(\mathbf{k}, \mathbf{r}) = \sum_{i=x,y,z} \frac{\hbar^2 (k_i - k_{is}^0)^2}{2 m_{is}^*(\mathbf{r})} \quad (2.3)$$

where,  $m_{iS}^*(\mathbf{r})$  is the effective mass of an electron or a hole along the  $i^{\text{th}}$  co-ordinate axes,  $k_{iS}$  is the  $i^{\text{th}}$  component of the wave vector  $\mathbf{k}_S$  corresponding to the minima of the conduction band or the maxima of the valence band, and  $W_{iS}(\mathbf{k}, \mathbf{r})$  will be called the  $i^{\text{th}}$  component of the kinetic energy  $W_S(\mathbf{k}, \mathbf{r})$ . The energy  $E_S(\mathbf{r})$  can be broken into two parts as<sup>5</sup>

$$E_S(\mathbf{r}) = E_{V\ell}(\mathbf{r}) - \chi_S(\mathbf{r}) \quad (2.4)$$

where,  $E_{V\ell}(\mathbf{r})$  is the energy of the local vacuum level and  $\chi_S(\mathbf{r})$  is the affinity of an electron or a hole.

We restrict our analysis to the steady state situation ( $(\partial f_S(\mathbf{k}, \mathbf{r}, t))/\partial t = 0$ ). In this case, with the help of Eqs. (2.2), (2.3) and (2.4), the steady state nonequilibrium distribution function  $f_S(\mathbf{k}, \mathbf{r})$  corresponding to the exact solution of the BTE (2.1) can be expressed as

$$f_S(\mathbf{k}, \mathbf{r}) = f_S^0(\mathbf{k}, \mathbf{r}) - \hbar\tau_S(\mathbf{r}) \sum_i \left[ -s \frac{(k_i - k_{iS})}{m_{iS}^*(\mathbf{r})} \mathbf{a}_i \cdot \nabla f_S(\mathbf{k}, \mathbf{r}) + \left\{ \frac{-e\mathbf{E}(\mathbf{r}) + \nabla\chi_S(\mathbf{r})}{\hbar^2} - s \frac{(k_i - k_{iS})}{2m_{iS}^*(\mathbf{r})} \nabla \ln m_{iS}^*(\mathbf{r}) \right\} \cdot \nabla_{\mathbf{k}} f_S(\mathbf{k}, \mathbf{r}) \right], \quad (2.5)$$

where,  $\mathbf{a}_i$  is the unit vector along the  $i^{\text{th}}$  co-ordinate axes and  $\mathbf{E}(\mathbf{r})$  is the electric field<sup>5</sup>

$$\mathbf{E}(\mathbf{r}) = \frac{1}{e} \nabla E_{V\ell}(\mathbf{r}) \quad (2.6)$$

It should be noted that  $\mathbf{E}(\mathbf{r})$  is the effective electric field because the energy of the local vacuum level may consist of other potential energies in addition to the electrostatic energy.

The electron or hole current density  $\mathbf{J}_S(\mathbf{r})$  can be obtained from its definition

$$\mathbf{J}_S(\mathbf{r}) = s e \int \mathbf{v}_S(\mathbf{k}, \mathbf{r}) f_S(\mathbf{k}, \mathbf{r}) d^3k \quad (2.7)$$

where  $\mathbf{v}_S(\mathbf{k}, \mathbf{r})$  is the electron or hole group velocity which from Eqs. (2.2) and (2.3) is given as

$$\mathbf{v}_s(\mathbf{k}, \mathbf{r}) = \frac{1}{\hbar} \nabla_{\mathbf{k}} \epsilon_s(\mathbf{k}, \mathbf{r}) = -s \sum_i \frac{\hbar(\mathbf{k}_i - \mathbf{k}_{is})}{m_{is}^*(\mathbf{r})} \mathbf{a}_i \quad (2.8)$$

On substituting  $f_s(\mathbf{k}, \mathbf{r})$  from Eq. (2.5) and  $\mathbf{v}_s(\mathbf{k}, \mathbf{r})$  from Eq. (2.8) in Eq. (2.7), we get

$$\begin{aligned} \mathbf{J}_s(\mathbf{r}) = e\tau_s(\mathbf{r}) \sum_{i,j} \int d^3k & \frac{\hbar^2(\mathbf{k}_i - \mathbf{k}_{is})}{m_{is}^*(\mathbf{r})} \mathbf{a}_i \left[ -s \frac{(\mathbf{k}_j - \mathbf{k}_{js})}{m_{js}^*(\mathbf{r})} \mathbf{a}_j \cdot f_s(\mathbf{k}, \mathbf{r}) \right. \\ & \left. + \left\{ \frac{-eE(\mathbf{r}) + \nabla \chi_s(\mathbf{r})}{\hbar^2} - s \frac{(\mathbf{k}_j - \mathbf{k}_{js})^2}{2m_{js}^*(\mathbf{r})} \nabla \ln m_{js}^*(\mathbf{r}) \right\} \cdot \nabla_{\mathbf{k}} f_s(\mathbf{k}, \mathbf{r}) \right] \quad (2.9) \end{aligned}$$

Marshak and van Vliet<sup>5</sup> have obtained the expressions for the electron and hole current densities by replacing the local nonequilibrium distribution function  $f_s(\mathbf{k}, \mathbf{r})$  on the right hand side (RHS) of Eq. (2.9) by the local equilibrium distribution function  $f_s^0(\mathbf{k}, \mathbf{r})$ . This replacement corresponds to the first order solution of the BTE. Here we shall obtain the generalized expressions for the electron and hole current densities from Eq. (2.9) in terms of local nonequilibrium averages of the components of the kinetic energies without making any approximation to the nonequilibrium distribution function  $f_s(\mathbf{k}, \mathbf{r})$ . The local nonequilibrium average of any arbitrary quantity  $A(\mathbf{k}, \mathbf{r})$  is defined as

$$A_s(\mathbf{r}) = \frac{\int A(\mathbf{k}, \mathbf{r}) f_s(\mathbf{k}, \mathbf{r}) d^3k}{n_s(\mathbf{r})} \quad (2.10)$$

where

$$n_s(\mathbf{r}) = \int f_s(\mathbf{k}, \mathbf{r}) d^3k \quad , \quad (2.11)$$

is the local density (or concentration) of electrons or holes.

The derivation of the generalized expressions for the electron or hole current densities proceeds as follows. The first term on the RHS of Eq. (2.9) is rearranged as

$$\begin{aligned}
 & \sum_{i,j} \frac{e\tau_s(\mathbf{r})}{m_{is}^*(\mathbf{r})} \mathbf{a}_i \mathbf{a}_j \cdot [-s] \int \frac{\hbar^2(k_i - k_{is})(k_j - k_{js})}{m_{js}^*(\mathbf{r})} \nabla f_s(\mathbf{k}, \mathbf{r}) d^3k \\
 &= -s \sum_{i,j} \mu_{is}(\mathbf{r}) \mathbf{a}_i \mathbf{a}_j \cdot \left[ \nabla \left( \frac{\hbar^2}{m_{js}^*(\mathbf{r})} \right) \int (k_i - k_{is})(k_j - k_{js}) f_s(\mathbf{k}, \mathbf{r}) d^3k \right. \\
 &\quad \left. - \nabla \left( \frac{\hbar^2}{m_{js}^*(\mathbf{r})} \right) \int (k_i - k_{is})(k_j - k_{js}) f_s(\mathbf{k}, \mathbf{r}) d^3k \right] = -2s n_s(\mathbf{r}) \sum_i \mu_{is}(\mathbf{r}) \mathbf{a}_i \mathbf{a}_i \cdot \\
 &\quad \cdot \left[ \nabla W_{is}(\mathbf{r}) + W_{is}(\mathbf{r}) \nabla \ln n_s(\mathbf{r}) + W_{is}(\mathbf{r}) \nabla \ln m_{js}^*(\mathbf{r}) \right], \quad (2.12)
 \end{aligned}$$

where

$$\mu_{is}(\mathbf{r}) = \frac{e\tau_s(\mathbf{r})}{m_{is}^*(\mathbf{r})} \quad (2.13)$$

is the mobility of the electrons or holes. In deriving Eq. (2.12), we have used the property of the cubic symmetry that

$$\begin{aligned}
 \int (k_i - k_{is})(k_j - k_{js}) f_s(\mathbf{k}, \mathbf{r}) d^3k &= \delta_{ij} \int (k_i - k_{is})^2 f_s(\mathbf{k}, \mathbf{r}) d^3k \\
 &= \frac{2}{\hbar^2} n_s(\mathbf{r}) m_{is}^*(\mathbf{r}) W_{is}(\mathbf{r}) \delta_{ij} \quad (2.14)
 \end{aligned}$$

By using the physical condition,

$$f_s(\mathbf{k}, \mathbf{r}) \rightarrow 0 \quad \text{as} \quad k \rightarrow \pm \infty,$$

of the distribution function  $f_s(\mathbf{k}, \mathbf{r})$ , the second term on the RHS of Eq. (2.9) can be integrated by parts as

$$\begin{aligned}
 & \sum_{ij} \frac{e\tau_s(\mathbf{r})}{m_{is}^*(\mathbf{r})} \mathbf{a}_i \int d^3k \hbar^2 (k_i - k_{is}) \left\{ \frac{-eE(\mathbf{r}) + \nabla \chi_s(\mathbf{r})}{\hbar^2} - s \frac{(k_j - k_{js})^2}{2m_{js}^*(\mathbf{r})} \nabla \ln m_{js}^*(\mathbf{r}) \right\} \cdot \\
 & \cdot \nabla_k f_s(\mathbf{k}, \mathbf{r}) = - \sum_{ij} \mu_{is}(\mathbf{r}) \mathbf{a}_i \int d^3k f_s(\mathbf{k}, \mathbf{r}) \nabla_k \cdot \left\{ \hbar^2 (k_i - k_{is}) \left\{ \frac{-eE(\mathbf{r}) + \nabla \chi_s(\mathbf{r})}{\hbar^2} \right. \right. \\
 & \left. \left. - s \frac{(k_j - k_{js})^2}{2m_{js}^*(\mathbf{r})} \nabla \ln m_{js}^*(\mathbf{r}) \right\} \right\} = - n_s(\mathbf{r}) \sum_i \mu_{is}(\mathbf{r}) \mathbf{a}_i \mathbf{a}_i \cdot
 \end{aligned}$$

$$[-e\mathbf{E}(\mathbf{r}) + \nabla\chi_s(\mathbf{r}) - 2s \sum_j W_{js}(\mathbf{r}) \nabla \ln m_{js}^*(\mathbf{r}) - s \sum_j W_{js}(\mathbf{r}) \nabla \ln m_{js}^*(\mathbf{r})] . \quad (2.15)$$

Now substituting Eq. (2.12) and (2.15) in Eq. (2.9) we obtain the generalized expressions for the electron and hole current densities as

$$\begin{aligned} \mathbf{J}_s(\mathbf{r}) = n_s(\mathbf{r}) \sum_j \mu_{js}(\mathbf{r}) \mathbf{a}_j \mathbf{a}_j \cdot [e\mathbf{E}(\mathbf{r}) - \nabla\chi_s(\mathbf{r}) + s \sum_j W_{js}(\mathbf{r}) \nabla \ln m_{js}^*(\mathbf{r}) \\ - 2s \sum_j W_{js}(\mathbf{r}) \nabla \ln n_s(\mathbf{r}) - 2s \nabla W_{is}(\mathbf{r})] \end{aligned} \quad (2.16)$$

The above Eq. (2.16), obtained from the exact solution of the BTE, can be very useful for the modelling of transport processes in presence of high electric field. The modelling can be done by assuming a plausible form for the local nonequilibrium averages of the components of the kinetic energies  $W_{js}(\mathbf{r})$ . We have done this in the next section to discuss the sources of the photovoltage in solar cells.

### III - SOURCES OF THE PHOTOVOLTAGE

For discussing the sources of the photovoltage in a solar cell, we assume that the electric current flows in the x direction along which there exist a built-in electric field  $E_x^0$ . Since in equilibrium both electron and hole current densities are zero, we obtain from Eq. (2.16) the built-in electric field  $E_x^0$  as

$$eE_x^0 = \frac{d}{dx} \chi_s - s \sum_j W_{js}^0 \frac{d}{dx} \ln m_{js}^* + 2s \sum_j W_{js}^0 \frac{d}{dx} \ln n_s^0 + 2s \frac{d}{dx} W_{xs}^0 . \quad (3.1)$$

In Eq. (3.1) the superscript 0 represents the equilibrium situation. For the sake of brevity here and hereafter position dependence of the physical quantities is suppressed. When the light falls on the solar cell, the equilibrium is disturbed and the built-in electric field  $E_x^0$  is changed to its new value  $E_x$ . This change in electric field  $E_x - E_x^0$ , called the photoelectric field, produces the photovoltage

$$V = \int_0^L (E_x - E_x^0) dx \quad (3.2)$$

where L is the thickness of the solar cell along the x direction.



To obtain the sources of the photovoltage, we consider the situation of maximum photovoltage, called the open circuit voltage  $V_{oc}$ , which occurs at the open circuit condition. Since in the open circuit condition the total current is zero, the summation of Eq. (2.16), for both electrons and holes gives us

$$\sum_s n_s \mu_{xs} \left[ eE_x - \frac{d}{dx} \chi_s + s \sum_j W_{js} \frac{d}{dx} \ln m_{js}^* - 2s W_{xs} \frac{d}{dx} \ln n_s - 2s \frac{d}{dx} W_{xs} \right] = 0 \quad (3.3)$$

From the above Eq. (3.3), the electric field  $E_x$  can be written as

$$E_x = \frac{1}{\sigma_x} \sum_s n_s \mu_{xs} \left[ \frac{d}{dx} \chi_s + 2s \left( -\frac{1}{2} \sum_j W_{js} \frac{d}{dx} \ln m_{js}^* + W_{xs} \frac{d}{dx} \ln n_s + \frac{d}{dx} W_{xs} \right) \right] \quad (3.4)$$

where

$$\sigma_x = e \sum_s n_s \mu_{xs} \quad (3.5)$$

is the conductivity of the solar cell material in the presence of light. Now substituting  $E_x^0$  from Eq. (3.1) and  $E_x$  from Eq. (3.4) in Eq. (3.2) and then rearranging the resulting expression, we get a general expression for the open circuit voltage as

$$V_{oc} = \int_0^L dx \sum_s \frac{\mu_{xs}}{\sigma_x} \left[ -e \Delta n_s E_x^0 + 2s \frac{d}{dx} \Delta(n_s W_{xs}) - s \sum_j \Delta(n_s W_{js}) \frac{d}{dx} \ln m_{js}^* + \Delta n_s \frac{d}{dx} \chi_s \right] \quad (3.6)$$

where  $\Delta F = F - F^0$  denotes the change in any arbitrary quantity  $F$  in presence of light. Eq. (3.6) outlines various sources of the photovoltage. The first term is the usual photovoltage due to built-in electric field  $E_x^0$ . The second term is due to the gradients of the change in the  $x$  component of the average kinetic energy densities  $n_s W_{xs}$ . Third and fourth terms arise due to the compositional grading i.e. the gradients of the effective masses and the affinities of electrons and holes.

The above Eq. (3.6) reduces to the earlier results<sup>2,3</sup> when the components of the average kinetic energy  $W_{js}$  are calculated from the Maxwell Boltzmann equilibrium distribution function. This replacement of exact nonequilibrium distribution function by the Maxwell Boltzmann equilibrium distribution function is valid only for low photoelectric field. For high photoelectric field, it is difficult to calculate the components of the average kinetic energy because of the difficulties involved in the solution of the BTE. A reasonable approximation for the average kinetic energy in presence of electric field had been considered by Blatekjaer<sup>6</sup>. According to this approximation  $W_{js}$  can be assumed to be a sum of two terms, one due to equilibrium thermal energy  $W_{js}^0$  and other due to drift velocity caused by the photoelectric field. Thus

$$W_{js} = W_{js}^0 + \frac{m_{js}^* v_{js}^2}{2} \quad (3.7)$$

In the first approximation, the group velocity  $v_{js}$  can be taken as the product of the mobility and the photoelectric field. Therefore (3.7) can be written as

$$W_{js} = W_{js}^0 + \frac{m_{xs}^* \mu_{xs}^2 (E_x - E_x^0)^2}{2} \delta_{j,x} \quad (3.8)$$

Substituting Eq. (3.8) in Eq. (3.6) we get

$$\begin{aligned} V_{oc} = & \int_0^L dx \sum_s \frac{\mu_{xs}}{\sigma_x} [-e\Delta n_s E_x^0 + 2s(W_{xs}^0 + \Delta W_{xs}) \frac{d}{dx} \Delta n_s - s \sum_j (W_{js}^0 \Delta n_s \\ & - n_s \Delta W_{xs} \delta_{j,x}) \frac{d}{dx} \ln m_{js}^* + \Delta n_s \frac{d}{dx} \chi_s + 2s\Delta n_s \frac{d}{dx} W_{xs}^0 \\ & + 2s\Delta W_{xs} \frac{d}{dx} n_s^0 + 4s\Delta n_s W_{xs} \frac{d}{dx} \ln \mu_{xs} + 4s\Delta n_s W_{xs} \frac{d}{dx} \ln \Delta E_x ] . \end{aligned} \quad (3.9)$$

Eq. (3.9) uncovers some additional sources of the photovoltage which do not appear in the approximate treatment<sup>2,3</sup> based on the first order solution of the BTE. These new sources are due to last three terms which depend on the gradients of the equilibrium concentration and mobilities of electrons and holes and the photoelectric field. It also shows that the

second term due to Dember potential and the third term due to gradients of the effective masses of electrons and holes depend on the photoelectric field. The fifth term due to gradient of the equilibrium thermal energy was not considered in the earlier treatments<sup>2, 3</sup>. The new sources, due to the last three terms, can be quite significant in solar cells of high mobilities of electrons and holes and high photoelectric field. Even for small electric field ( $\Delta W_{js} \approx 0$ ). Eq. (3.9) is an improvement to the earlier expression<sup>2, 3</sup> due to the presence of equilibrium thermal kinetic energies  $W_{js}^0$ . These kinetic energies can be evaluated by considering any local equilibrium distribution function (for example Maxwell-Boltzmann or Fermi-Dirac distribution functions). In earlier treatments local equilibrium distribution function is taken as the equilibrium Maxwell-Boltzmann distribution function.

#### IV - CONCLUSION

The principal result of this work is a general expression for the open circuit voltage of a solar cell employing inhomogeneous semiconductors. This expression is obtained from the generalized expressions for the electron and hole current densities which can be very useful for modelling of the semiconductor devices in high electric field. Some new sources of the photovoltage have been discovered. These sources, which can be important for the high electric field and high mobilities of electrons and holes, arise from the gradients of the equilibrium concentrations and mobilities of electron and holes and the photoelectric field.

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TÍTULO

The Sources of photovoltage in solar cells (40)

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