Efficiency of thin film photocells

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We propose a new concept for the design of high-efficiency photocells based on ultra-thin (sub-micron) semiconductor films of controlled thickness. Using a microscopic model of a thin dielectric layer interacting with incident electromagnetic radiation we evaluate the efficiency of conversion of solar radiation into the electric power. We determine the optimal range of parameters which maximize the efficiency of such photovoltaic element.

Improvement of efficiency of semiconductor photovoltaic elements (solar cells) has been an important technological challenge for several decades. The maximum possible efficiency obtainable when every incident photon generates an electron-hole pair, which then separates into electron flowing to cathode and hole flowing to anode[1]. The limitations that reduce the efficiency of the practical solar cells relative to the ideal are 1) light reflection at the interfaces, 2) incomplete absorption of light entering the device due to finite thickness, 3) electron-hole relaxation inside the absorbing medium during diffusion to the leads[2, 3]. Interplay between two latter mechanisms leads to an existence of an optimal device thickness, typically a few optical wavelengths. Here we show that the interface reflection, commonly considered a completely independent loss mechanism, shows an interesting interplay with absorption in ultra-thin film devices. This opens a possibility for a new generation of ultra-thin (sub-wavelength) photovoltaic elements with efficiencies rivaling the best conventional devices.

A “working body” of a solar cell is typically a semiconductor with relatively high absorption index at frequencies corresponding to those of the sun quanta \( h \nu_{\text{sun}} \sim k_B T_{\text{sun}} \), \( T_{\text{sun}} \approx 6000 \, K \). Such semiconductors, however, process a rather high refraction index \( n \) at these frequencies. As a consequence, a fraction \( (n - 1)^2 / (n + 1)^2 \) of the incident light is reflected from the surface of the thin device. To reduce this loss, often anti-reflective coating are applied to the surface of the device. On the other hand, for sub-wavelength thin films, the reflection can be significantly smaller (for a reason similar to why even metallic films are transparent when thin enough). Thus reducing the film thickness one should reach an optimum where reflection is reduced but the absorption is still significant.

Also, in such thin devices the carrier recombination is naturally reduced. Electron-hole recombination which prevents efficient charge separation in the photocell is a major limiting factor in device operation. There are numerous mechanisms which lead to the charge relaxation in a bulk of a semiconductor. These mechanisms include spontaneous emission as well as phonon or impurity induced relaxation. While it is difficult to control these processes in the bulk of a semiconductor, it is clear that their contribution can be significantly reduced if diffusion length of electrons and holes is large compared to the width of the semiconducting layer.

Diffusion length for most semiconductors used in photovoltaics is of the order of a few microns. Since this distance is comparable to a typical wavelength of the sunlight, one could expect that the specific absorption (the ratio of the absorbed power to the incident power of radiation) in such a thin semiconducting layer is insufficient for any practical use. In order to see whether this is the case, it is instructive to look at the absorption of radiation in a layer of thickness \( d \), e.g. Fig. 1(a,b). For simplicity we assume that the radiation is incident perpendicular to the surface of the layer and is monochromatic with wavelength \( \lambda \). The layer has a dielectric constant whose real and imaginary parts are \( \epsilon_{\text{Re}} \) and \( \epsilon_{\text{Im}} \) respectively. The specific absorption of the dielectric layer can be easily evaluated by solving the wave equation \( (n/c^2) \hat{A} = \partial^2 \hat{A} / \partial z^2 \) \( (A \) is radiation field vector-potential, \( n = \epsilon^{1/2} \) is the refraction index, and \( c \) is the speed of light) in the three regions, i.e., Fig. 1(b), and taking into account the continuity conditions at the boundaries of the dielectric layer, \( A_1 = A_2 \), \( A_2 = A_3 \), \( \partial_z A_1 = \partial_z A_2 \), etc. After straightforward algebra one finds that the specific absorption is
$P_{\text{abs}} = 1 - |t|^2 - |r|^2$, where the amplitudes of transmitted and reflected waves are
\[ t = \frac{4n \exp(i\lambda)}{(n+1)^2 \exp(-i\lambda/\lambda) - (n-1)^2 \exp(i\lambda)}, \] \[ r = \frac{(n+1)^2 \exp(-i\lambda/\lambda) - (n-1)^2 \exp(i\lambda)}{(n+1)^2} \]

The specific absorption evaluated according to the above equations is presented in Fig. 2 for a GaAs slab as a function of its thickness $d$. GaAs has a relatively narrow ($\sim 1.4$ eV) bandgap and therefore is widely used in high-efficiency photocells. Since dielectric function of GaAs is strongly frequency dependent [4], in Fig. 2 we plot the specific absorption for several energies typical to the quanta of solar radiation. The 2 eV curve corresponds to the relatively low imaginary part of the dielectric constant and thus saturates slowly exhibiting several oscillations due to the interference between reflected and transmitted components. The 3 eV and 4 eV curves correspond to much higher absorption (for example $\epsilon_{\text{GaAs}}^{\text{GaAs}}(3 \text{ eV} \approx 17)$ and saturate much faster. Prior to saturation both curves exhibit a peak (again due to the interference) at roughly $d \approx \lambda/|\epsilon|$. Remarkably the value of the specific absorption at the peak ($\approx 0.42$ at $d \approx \lambda/|\epsilon| \approx 20 \text{ nm}$ for 3 eV curve) is nearly the same as its saturation value ($0.51$ at $d \gg \lambda$). Thus we conclude that the solar radiation can be absorbed by a semiconducting layer of submicron thickness almost as efficiently as by an infinitely thick slab.

In this paper, following the simple above considerations, we propose a new concept for the design of photovoltaic elements based on thin semiconductor films of controlled thickness. To put our arguments on a more rigorous footing in the following we consider a detailed microscopic model of a dielectric layer interacting with solar radiation. Effective Hamiltonian can be derived from standard quantum-mechanical interaction between matter and radiation, \((e/mc)\mathbf{A}(\mathbf{r}) \cdot \mathbf{p} + (e^2/2mc^2)\mathbf{A}^2(\mathbf{r})\), where here and in the following we assume Coulomb gauge for the electromagnetic field. The radiation induces transitions between valence and conduction band of the semiconductor. We assume that the temperature of the semiconductor is 0, and therefore these are the only possible transitions in the system (the valence band is completely full and the conduction band is empty). Denoting the Bloch states for the valence/conduction bands as $\psi_{\mathbf{k}}^{(v,c)}(\mathbf{r}) = \exp(-i\mathbf{k}\mathbf{r})\psi_{\mathbf{k}}^{(v,c)}(\mathbf{r})$, $H_0\psi_{\mathbf{k}}^{(v,c)} = E_{\mathbf{k}}^{(v,c)}\psi_{\mathbf{k}}^{(v,c)}$ ($H_0$ is a Hamiltonian of the crystal in the absence of coupling to radiation field) one can rewrite the radiative transition Hamiltonian in terms of single particle states in the semiconductor as

\[ H_{\text{int}} = \frac{e}{mc} \sum_{\mathbf{k},\mathbf{q},\alpha} \langle u_{\mathbf{0}}^{v}(p) | u_{\mathbf{0}}^{v} \rangle c_{\mathbf{k}}^{+} d_{\mathbf{k} - \mathbf{q} + \alpha} A_{\mathbf{q} - \alpha}^{z = 0} + \text{H.c.} \]

We make the following assumptions: (1) While the electromagnetic field does not significantly vary with distance inside the film, the electronic wave-functions are effectively 3-dimensional - we assume that $\lambda_{\text{sun}} \sim 2\pi c/(k_B T_{\text{sun}}) \gg d \gg h/(m^* E_g)^{1/2}$, where $d$ is the thickness of the film, $m^*$ is exciton effective mass, $(m^*)^{-1} = m_v^{-1} + m_c^{-1}$, $m_c$ and $m_v$ are effective masses in valence and conduction bands, and $E_g$ is the band-gap (in this paper we assume that bands have extrema at zero momentum). This assumption allows one to carry out an analytic calculation with rather simple and transparent results. We will discuss the validity of this approximation at the end of the paper; (2) The bands have different symmetry, say $s$ and $p$, so index $\alpha$ denotes angular momentum of an electron in $p$ band. Since wave-vectors of the incident radiation are nearly perpendicular to the surface of the film and the film is assumed infinite in $x - y$ dimension, only in-plane components of the angular momentum ($\alpha = x, y$) are relevant in Eq. (2); (3) The coupling in Eq. (2) is isotropic and the coupling constant $t_\alpha = \langle u_{\mathbf{0}}^{v}\rangle (\mathbf{p}) | u_{\mathbf{0}}^{v}\rangle \approx E_g/(cs^2)$, where $c$ is the dipole moment per unit cell of the film and $S$ is the surface area of the film. (4) Due to external electric load the bands have effectively different chemical potentials, $\mu_n$ and $\mu_p$, e.g., Figs. 1(c) and 1(d). That is, once electron is promoted from valence to conduction band, it immediately "rolls over" to the left lead, which corresponds to the infinite transition rate between the semiconductor and the metallic lead (an infinitely thin Shottky barrier). Clearly, were the rate comparable or slower than the electron-hole relaxation rate, the efficiency of the cell would have decreased. (5) The $p - n$ junction is prepared (doped) as shown in Fig. 1(c) - the top of the valence band in the $p$-doped area of the junction lies just below the bottom of the of the conduction band in the $n$-doped area. Therefore the maximum voltage the photo-cell can sustain is equal to $E_g/e$, which corresponds to the assumption of maximum efficiency of Shockley and Quassar [1] to each electronic transition from valence to conduction band generates energy $E_g$ in the circuit. The photocurrent is defined as the rate of the charge transfer between the valence and conduction band, $I_{ph} = |H_{\text{int}}, \sum_{\mathbf{k},\alpha} c_{\mathbf{k}}^{+} c_{\mathbf{k}}|$. To the lowest non-vanishing order it can be expressed as

\[ I_{ph} = -\frac{ie}{\hbar} \sum_{\mathbf{k},\alpha} \langle \mathbf{q} | \mathbf{A}^{\alpha} / \mathbf{q} | \mathbf{E}^{\alpha} / \mathbf{q} \rangle. \]
Moreover, due to self-energy defined for the bulk of the semiconductor. Since \( \Sigma \) depends only on closed form equation for \( \Sigma \) of incident radiation.

\[ \text{FIG. 2: Specific absorption of GaAs slab as a function of its thickness. Different curves correspond to different frequencies (energies) of incident radiation.} \]

In order to incorporate effects of absorption and reflection from the film, it is necessary to include renormalization of the photon Green’s function due to interactions with the film according to Eq. (2). These effects can be treated by means of Dyson equation, which, for the case of two-dimensional film reads

\[
\hat{D}_{\alpha\beta} (\omega, q, z) = \hat{D}_{0\alpha\beta} (\omega, q, z) + \hat{D}_{0\alpha\gamma} (\omega, q, z) \Sigma_{\gamma\delta} (\omega, q, z) \hat{D}_{\delta\beta} (\omega, q, z),
\]

where hats denote the standard 2 × 2 matrix structure of the non-equilibrium Green’s functions. The self-energy \( \Sigma_{\gamma\delta} \) in Eq. (1) is quasi-two-dimensional. Since \( l \gg \hbar/(m^* E_0)^{1/2} \), effects related to the finite width of the semiconducting slab can be neglected and \( \Sigma_{\gamma\delta} (\omega, q, z) = \sum_q \Sigma_{\gamma\delta} (\omega, q) \), where \( \Sigma_{\gamma\delta} (\omega, q) \) is the self-energy defined for the bulk of the semiconductor. Moreover, due to \( x - y \) symmetry \( \Sigma_{\gamma\delta} \) reduces to a \( \delta_{\gamma\delta} \Sigma \), where \( \Sigma \) depends only on \( |q| \). Therefore we obtain a closed form equation for \( \hat{D}_{\alpha\beta q, z} (\omega, z = z') = 0) \):

\[
\hat{D}_{\alpha\beta}(0, 0) = \hat{D}_{0\alpha\beta}(0) + \hat{D}_{0\alpha\gamma}(0) \Sigma_{\gamma\beta}(0, 0),
\]

where components of the bare Green’s function \( \hat{D}_{0\alpha\beta} \) for solar radiation are:

\[
\hat{D}_{0\alpha\beta} (\omega, q, z) = \sum_q \frac{4\pi (\delta_{\alpha\beta} - q_n q_\beta/q^2)}{\omega^2 - c_n/2 (1 + i\delta)},
\]

\[
\hat{D}_{\alpha\beta} (\omega, q, z) = \sum_q \frac{4\pi q_n^2}{\omega^2} \left( \delta_{\alpha\beta} - q_n q_\beta/q^2 \right) \times [\delta(\omega - \omega_n n_q - \delta(\omega + \omega_n)(1 + n_{-q})].
\]

In Eq. (9) \( \omega_q = \hbar c |q| \) and the \( n_q \) is the distribution function of solar radiation. We assume that the incident radiation wavevectors are uniformly distributed within a cone with an opening angle \( 2\phi (\phi \ll 1) \). Moreover, in order for the incident power to be maximum, we assume that the surface of the cell is perpendicular to the cone’s axis. Then \( \tilde{n}_q = n^B \theta(q_z) \theta(\phi q_z - |q|_n) \), where \( n^B_q \) is Bose distribution function with temperature \( T_{\text{sun}} \).

Furthermore due to the homogeneity of the Green’s function \( \hat{D}_{\alpha\beta q} \), in \( x - y \) plane one can seek for solution of Eq. (5) in the form \( \hat{D}_{\alpha\beta} = \hat{D}_1 \delta_{\alpha\beta} + \hat{D}_2 q_i q_\beta/q^2 \), where \( \hat{D}_1(2) \) are \( 2 \times 2 \) matrices in the Keldysh space, but depend only on the absolute value of the wavevector \( q \). Substitution of this ansatz into Eq. (6) yields two independent equations for \( \hat{D}_1 \) and for \( \hat{D}_3 = \hat{D}_1 + \hat{D}_2 \). After solving those equations one finds

\[
\hat{D}_1(3) = \left( \frac{D_R^{01(3)}}{(D_1^{01(3)})^{-1} - \Sigma R(A)} \right)^{-1},
\]

where \( \hat{D}_{01} \) is the diagonal part of \( \hat{D}_{0\alpha\beta} \), e.g., Eqs. (6), and \( \hat{D}_{00} = \hat{D}_{01} + \hat{D}_{02} \), where \( \hat{D}_{02} \) is the transverse part of \( \hat{D}_{0\alpha\beta} \). \( \Sigma R(A) \) and \( \Sigma < \) are retarded(advanced) and “lesser” parts of photon self-energy. Also we find a standard expression for the retarded(advanced) Green’s functions of the radiation:

\[
\hat{D}_1^{R(A)} = \left( [D^{R(A)}]^{-1} - \Sigma R(A)]^{-1} \right.
\]

We can now evaluate the photo-current in Eq. (3) in terms of the Green’s function of Eq. (7). The first contribution is due to absorption of incident radiation accompanied by transfer of electrons from valence to conduction band. It comes from the first term in the numerator in the RHS of Eq. (7). This term can also lead to the reverse current due to spontaneous and stimulated emission, i.e., transitions from conduction band to the valence band accompanied by creation of a real photon. It arises due to the \( \delta(\omega + \omega_q n_q) \) term in Eq. (6b). This process is, however, not allowed while the energy gap \( E_g \) exceeds the applied voltage \( V_n = \mu_p \), e.g., Fig. 1(c,d). In this situation the cell becomes a light-emitting diode, and, as was stated above, we are not interested in such case in this paper.

The second contribution comes from the \( \Sigma < \) term in the RHS of Eq. (7). It corresponds to the emission of virtual quanta of radiation by one electron-hole pair and their subsequent re-absorption by another pair, resulting in an incoherent simultaneous transfer of two electrons from conduction to valence band. This process gives a reverse contribution to the current which, once again, is non-zero only in the “light-emitting” regime (or at high temperature).

The self-energies in Eqs. (7,8) can be evaluated in terms of the electronic Green’s functions. The leading contribution comes from the conventional polarization diagram, i.e., a convolution of two electronic Green’s func-
tions. For non-equilibrium situation one obtains
\[
\Sigma^R(\omega, 0) = \frac{it^2}{4\pi} \sum_k \int \frac{d\omega'}{2\pi} G^K_{vk}(\omega + \omega') G^R_{ck}(\omega') \\
+ G^R_{vk}(\omega + \omega') G^R_{ck}(\omega') + (v \leftrightarrow c),
\]
and $\Sigma^A = (\Sigma^R)^\ast$. In Eq. (9) $G^R(A)$ are retarded (advanced) Green's functions of valence(conduction) electrons and $G^K_{vk}$ is the Keldysh Green's function. Note that in Eq. (8) we evaluated the self-energy at zero wavevector, since photon wavevectors are small compared to those of electrons, and therefore the self-energy $\Sigma$ is weakly dependent on $q$ for direct bandgap materials.

The self-energies $\Sigma^{(R/A)}_{\text{im}}$ can be easily evaluated for non-interacting electrons. Then $G^R_{vk}(\omega) = (\omega - E_{vk}^{(c)} + i\delta)^{-1}$ and $G^K_{vk}(\omega) = (1 - 2n^{F}_{n(p)k})\delta(\omega - E_{vk}^{(c)})$, where $n^{F}_{n(p)k}$ are Fermi filling factors. The valence and conduction electrons are assumed to have chemical potentials corresponding to those of the two leads, $\mu_n$ and $\mu_p$ respectively. For these Green's functions the imaginary part of the self-energy yields:
\[
\Sigma^{R(A)}_{\text{im}}(\omega, 0) = \pm \frac{a g^2}{2\pi} \Theta(\omega - E_g) \sqrt{\omega - E_g},
\]
where we have introduced a dimensionless parameter $a = g^2 d E_g^3 / (m^* 3/2 / 21/2 h^3 c)$. A similar calculation for the real part of $\Sigma^{R(A)}$ yields an ultraviolet divergence. This, however, is an artifact of our approximation of the infinitely thin absorbing layer (similar problem occurs in the quantum electrodynamics treatment of electron-photon interaction). In a proper microscopic theory this divergence in the real part of the self-energy is exactly cancelled by the $e^2 A^2(r)/(2 m c^2)$ term in the radiation-matter interaction Hamiltonian (the frequency sum rule). Taking into account this cancellation is equivalent to performing the Kramers-Krönig transformation on the dielectric function $\text{Re} \epsilon(\omega) = 4\pi e^2 \text{Re} \Sigma(\omega)/\omega^2$, rather than self-energy:
\[
\Sigma^{R(A)}_{\text{re}}(\omega, 0) = \frac{\omega^2}{\pi} P \int \frac{\omega^2(\omega, 0)d\omega'}{\omega^2(\omega - \omega')} = \frac{a g^2}{2\pi} \left( 2 \sqrt{E_g - \sqrt{\omega + E_g} - \sqrt{\omega - E_g}} \right),
\]
where we introduced another dimensionless parameter $b = E_g/T_{\text{sun}}$. Function $\eta_{\text{max}}(a, b)$ shown in Figure 3 has a pronounced maximum at $a \simeq 2.0$ and $b \simeq 2.4$. This maximum corresponds to the first maximum of the specific absorption curves in Fig. 2. Note that since our microscopic theory is valid only for thin dielectric layers ($d \ll \lambda_{\text{sun}}$), it does not account for the saturation of specific absorption at larger thickness, i.e., when $d > \lambda$. However, since $\eta_{\text{max}}$ reaches maximum at $d \sim \lambda_{\text{sun}}/c_0$, our theory is fully self-consistent for semiconductors with sufficiently high value of the dielectric constant.

FIG. 3: Dependence of photovoltaic efficiency on dimensionless parameters $a$ and $b$.

Since the photo-current is only weakly dependent on voltage for $V < E_g$ and becomes negative due to spontaneous and stimulated emission emission for $V > E_g$, we have $(IV)_{\text{max}} \simeq I_{ph} E_g / e$. The incident power per unit area $P_{\text{in}} = c u$, where energy density $u = (2/v) \sum_q \hbar \omega_q n_q$, where $v$ is the mode quantization volume and factor 2 is due to two polarizations of the light waves. Carrying out the calculation we obtain the following closed form expression for the maximum photovoltaic efficiency of the cell:
\[
\eta_{\text{max}} = \frac{30 a b^4}{\pi^4} \int_1^\infty \frac{dx}{\exp(bx) - 1} \times \frac{x^3 - 1}{(x + a \sqrt{x} - 1)^2 + a^2 (2 - \sqrt{x} + 1 - \sqrt{x - 1})^2},
\]
where $a$ and $b$ are defined in Eqs. (10) and (11). One can evaluate the photocurrent $I_{ph}$ given by Eq. (3) in this paper we are interested in the maximum efficiency of the photocell, which can be defined as $\eta_{\text{max}} = (IV)_{\text{max}}/P_{\text{in}}$, where $(IV)_{\text{max}}$ is the power that is dissipated in the circuit assuming an optimal load and $P_{\text{in}}$ is the power of incident solar radiation.
$\epsilon_{\text{opt}} \simeq \frac{1.2hc}{E_{\text{opt}}^0(\epsilon_0^{G_{\text{GaAs}}} - 1)} \simeq 15 \text{ nm}$, which is within the fabrication capabilities of contemporary molecular beam epitaxy technology. Another promising material is amorphous Silicone which, unlike crystalline Si, has large imaginary part of dielectric constant [6]. Moreover, in ultra-thin devices considered here, the thermal equilibration of photo-generated carriers may occur on the time scales longer than the charge separation timescale. Thus the hot-carrier physics [7] may lead to further enhancement of the efficiency.

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