# Impurity Photovoltaic Effect

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Impurities with energy levels somewhere in between the valence and conduction bands of a semiconductor can provide additional stepwise transitions from the valence to the conduction band by the subsequent absorption of two or more photons with energies less than the band gap. This was first recognised by M.Wolf [1], who found a great improvement in the efficiency of solar cells by the incorporation of impurities. His calculations are, however, too optimistic. They use a constant minority carrier lifetime irrespective of the presence of impurities. This approach violates microscopic reversibility since it makes use of carrier generation via impurity transitions but disregards recombination mediated by impurities.

Our calculation is based on radiative transitions only. It shows that the generation rate of electron-hole pairs is increased by additional impurity transitions but that the recombination rate is increased as well. Although the recombination is assumed to be entirely radiative, the theoretical efficiency of materials with band gaps below 1.2 eV decreases due to the presence of impurities. For larger band gaps, however, the theoretical efficiency is improved by impurity transitions and large band gap materials become attractive for solar cells. In our calculation optimal use is made of the incident spectrum. For one impurity level at energy $\varepsilon_1$ all photons with energy $\varepsilon_1 - \varepsilon_V < h\nu < \varepsilon_C - \varepsilon_1$ are assigned to the transition from the valence band to the impurity level, all photons with energy $\varepsilon_C - \varepsilon_1 <$

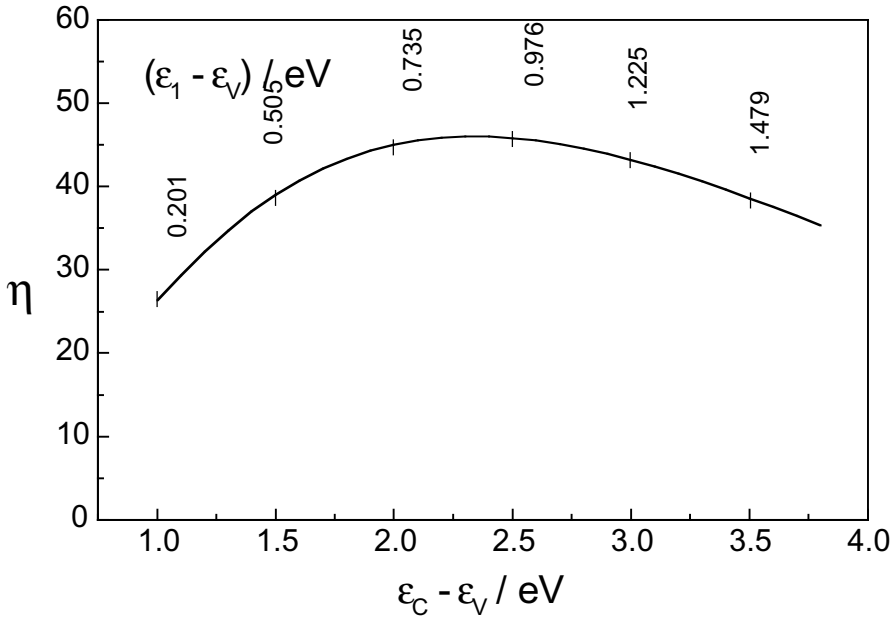


Fig 1 Efficiency $\eta$ as a function of the band gap $\varepsilon_C - \varepsilon_V$ for AM0 radiation for materials containing impurities with a single optimised level at $\varepsilon_1$.

$h\nu < \varepsilon_C - \varepsilon_V$ are assigned to the transition from the impurity level to the conduction band and photons with $h\nu > \varepsilon_C - \varepsilon_V$ are assigned to band-band transitions. Fig. 1 shows the efficiency as a function of the band gap for an optimal value of a single impurity level. A maximal efficiency of 46% is found for a band gap of 2.3 eV and an impurity level at $\varepsilon_1 = 0.88$ eV above the valence band.

Wolf [1] suggested that the efficiency may be improved even more by introducing more than one impurity level. He assumes an absorptivity of $\alpha = 1$ for each transition. For a transition from the valence band into the impurity this would require that the impurity is almost empty. For a transition from the impurity into the conduction band, however, the impurity should almost be fully occupied. The optimal situation for the absorption of all potentially absorbable photons is achieved if one half of the impurity states at each energy level is occupied and one half is empty, allowing transitions into the impurity state and out of the impurity state with equal probability. With a single impurity level this condition can be realised by proper doping. Charge neutrality ensures that the occupation of the impurity state will not change markedly by illumination.

The occupation of impurities is different if more than one impurity level is present. The lower energy level will always be more strongly occupied than the higher energy level, even under illumination. The absorption properties are in general quite different for different transitions. If small absorption coefficients are compensated by a larger thickness of the material, total absorption of all absorbable photons can be achieved For two impurity levels a maximal efficiency of 50.3% is found for a bandgap of 3 eV and impurity levels at $\varepsilon_1 = 0.46$ eV and at $\varepsilon_2 = 1.44$ eV. For impurity concentrations of $2 \cdot 10^{18}/cm^3$, however, the absorption coefficient of some transitions is so small that total absorption requires an unrealistic thickness of 1 cm.

For a more realistic thickness of 100 µm, the maximal efficiency for two impurity levels with a concentration of $2 \cdot 10^{18}/cm^3$ each, is only 34.7% and is found for a bandgap of 2.0 eV and impurity levels at $\varepsilon_1 = 0.39$ eV and at $\varepsilon_2 = 0.78$ eV. This is a much smaller efficiency than found for one impurity level where the same concentration results in total absorption for a thickness of only 10 µm.

We can conclude that a single impurity level may improve the efficiency of solar cells, but more than one impurity level is unfavourable. This is even more so if non-radiative transitions are considered which are more likely if more different energy levels are available.

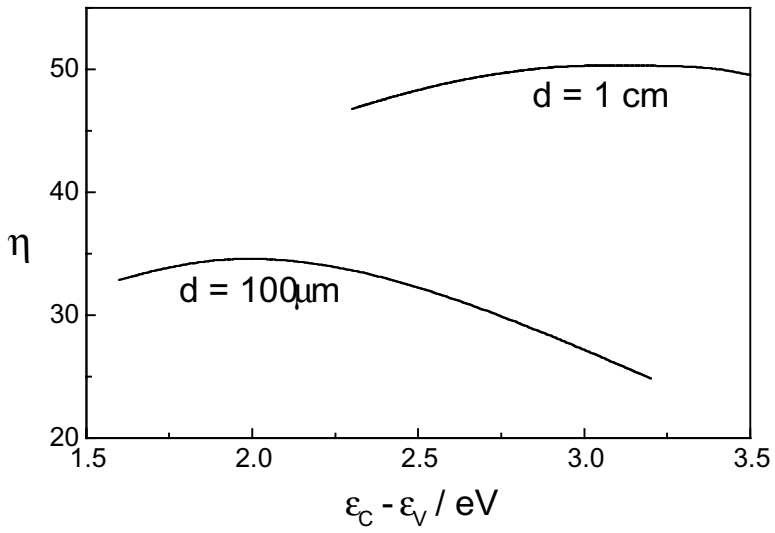


Fig. 2 Efficiency η for AM0-radiation and radiative transitions involving two impurity levels

[1] M. Wolf, Proc. IRE, **48** (1960) 1246