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A. P. Kirk

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Analysis of quantum coherent semiconductor quantum dot *p-i-n* junction photovoltaic cells

A. P. Kirk

Department of Materials Science and Engineering
University of Texas at Dallas
Richardson, TX 75080, USA

Abstract

A recent hypothesis (May 2010) indicates that the power conversion efficiency of a semiconducting *p-i-n* junction photovoltaic (PV) cell with an intrinsic region consisting of quantum dots can be increased by using quantum coherence to break detailed balance. The limitations of this hypothesis are shown here.

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It has been suggested by Scully [1] that it is possible to suppress radiative recombination and break detailed balance by using quantum coherence, which in turn is supposed to lead to increased power conversion efficiency in a semiconducting *p-i-n* junction quantum dot photovoltaic (PV) cell where the quantum dots are in the intrinsic region. Although this appears to be a promising development, a systematic analysis presented here highlights the limitations of this hypothesis.

Scully shows in [1] that the maximum attainable photovoltage, V, of a *p-i-n* junction quantum dot PV cell (see Fig. 1a in [1]) is given by the thermodynamic Carnot-cycle limit as

$$V = \frac{\hbar \nu}{q}\left(1 - \frac{T_a}{T_s}\right) \qquad (1)$$

where $\hbar\nu$ is the incident photon energy, T_a is the ambient (PV cell) temperature, T_s is the temperature of the sun, and q is the electronic charge. Equation (1) that Scully reports in [1] was previously reported by Rose [2] in 1960 to express maximum photogenerated voltage.

However, the actual *p-n* junction bandgap energy, E_g, or more specifically the quasi Fermi level (E_{Fn}, E_{Fp}) separation (i.e. difference in chemical potential energy, $\Delta\mu$) written as

$$V = \left(E_{F_n} - E_{F_p}\right)/q \quad (2)$$

actually determines the photogenerated voltage V of a PV cell [3] rather than Eq. (1) as outlined by Scully. Although this may seem subtle at first, understanding that the maximum voltage of a semiconductor *p-n* (or *p-i-n*) junction PV cell – the type of PV cell discussed by Scully – is a function of the bandgap, and more precisely a function of the quasi Fermi levels, is a critical distinction.

Next, Scully suggests a mechanism to achieve a level of quantum efficiency (the term quantum efficiency here refers to a quantum mechanical-based efficiency rather than the classic thermodynamic efficiency) which exceeds the voltage of Eq. (1) as

$$V = \frac{\hbar\nu}{q}\left(1 - \frac{T_a}{T_s}\right) + \frac{\hbar\nu_0}{q} \quad (3)$$

where,

$$\hbar\nu_0 = \tfrac{1}{2}\left(E_{c_1} - E_{c_2}\right), \quad (4)$$

and E_{c1} and E_{c2} represent upper level c_1 and c_2 conduction band states of the quantum dots located in the intrinsic layer of the semiconducting *p-i-n* junction PV cell. Equation (4) represents additional energy due to quantum coherence. Therefore, Scully is arguing that he has identified a PV cell that can now generate more power than that which is radiated from the sun by adding on Eq. 4 (this will be discussed again later in this Letter in the context of Scully's proposed use of the Fano effect to generate the energy term given in Eq. 4). Clearly, this is not possible. Rose's work [2] was in response to what was known as the Shockley paradox, proposed by Shockley at the 1951 AAAS meeting in Philadelphia. Rose proved in 1960, and Shockley later acknowledged in his 1961 work on the detailed balance limiting efficiency [4], that a PV cell cannot generate more power than what is supplied to a semiconducting *p-n* junction from the incident solar radiation.

Scully's proposal appears to be an incomplete version of a concept known as the 'hot carrier PV cell' [3]. It is thought that to make a hot carrier PV cell function properly, energy selective contacts (e.g. a resonant tunneling barrier) to the portion of the cell where hot electrons (and holes) are generated must be available, along with slowed carrier cooling, in order to prevent what would otherwise be rapid thermalization loss of the more energetic carriers [5]. Notably (see Fig. 1a and 1b in [1]), the contacts in Scully's proposed PV cell are only connected to the *p*- and *n*-type semiconductor regions. In other words, there is no provision for energy selective contacts that specifically interact with the intrinsic quantum dots, thus allowing extraction of the hot, more energetic electrons that may then possibly lead to an increase in photogenerated voltage (apparently from Fig. 3a in [1] there are no corresponding hot holes). It is known, however, that lower bandgap energy quantum dots located in the intrinsic region of a *p-i-n* junction PV cell may allow for the absorption of photons with energy less than the *p-n* junction bandgap energy and this can lead to an increase in the photogenerated current of the PV cell.

Scully also indicates in [1] that there is a relation between the physics of his proposed photo-Carnot quantum heat engine [6] and the proposed quantum coherent *p-i-n* junction quantum dot PV cell (presented in [1]). The key component of the photo-Carnot quantum heat engine is the concept of a new, specialized, coherent working fluid: "phaseonium" [6]. Sunlight (the working fluid analog to "phaseonium") is incoherent and thus does not adopt "phaseonium" characteristics. This, in turn, renders the implied connection between increased solar PV efficiency and any similarity to the photo-Carnot quantum heat engine void.

In order to achieve quantum coherence, and thus the additional term $\hbar \nu_0$, Scully initially proposes the use of an external drive field. In the context of an actual solar PV cell deployed in the field, this concept of an external drive source would be impractical and inefficient. As one example, Scully (see Fig. 2b in [1]) shows an external microwave drive source coupling the two upper electron levels in a three-level system and states that this leads to a canceling of emission. In order to circumvent the use of an external drive field, Scully then states that Fano coupling (Fano interference effect) could be used instead of an external drive source to create quantum coherence between upper states c_1 and c_2 and achieve the additional energy term equivalent to Eq. 4. As stated earlier, it is not possible to extract more power out of a PV cell than what is radiated from the sun, regardless of whether or not quantum coherence is utilized. Moreover, as Harris shows in his 1989 work on lasing without inversion [7], Fano interference (coupling) effect does not break detailed balance. Taking quantum interference into consideration, constructive interference can occur leading to enhanced absorption as reported by Faist in 1997 for a combination deep/shallow semiconducting quantum well structure in which a thin tunneling barrier is located between the shallow quantum well and the continuum [8]. Nonetheless, constructive quantum interference implies an enhanced optical absorption coefficient (wavelength specific) rather than enhanced absorption being indicative of a fundamental breaking of detailed balance. As an aside, high efficiency Si PV cells have been designed with front-side texturing and anti-reflection coatings as well as back-side mirror layers [9] in order to enhance optical absorption (sometimes referred to as light trapping and photon recycling) thus managing the inherently low optical absorption coefficient of indirect bandgap Si. Enhanced photon absorption in highly engineered Si PV cells has resulted in improvement in power conversion efficiency yet has not resulted in a departure from detailed balance.

Furthermore, the key point from Shockley and Queisser's [4] work on detailed balance limit is that radiative recombination imposes an upper limit to minority carrier lifetime. Semiconducting *p-n* (or *p-i-n*) PV cells are minority carrier bipolar devices and thus both electron and hole lifetimes must be taken into consideration. It is not clear how quantum coherence in an intrinsic region of quantum wells or quantum dots will extend minority carrier lifetime in the *p-n* junction semiconductor where most of the incident solar photons are absorbed (see Fig. 3a in [1]).

Finally, for any quantum mechanical system interacting with its environment, which is the case for a quantum dot PV cell, quantum decoherence occurs. Even assuming no perturbation due to measurement, quantum decoherence will add an additional entropy component, ΔS_{QD}, as explained by Lloyd [10] to the existing initial entropy, S_{in}, of the system. Therefore, the theoretical efficiency (reverting to the thermodynamic limit) should be written as,

$$\eta = \left[1 - \frac{T_a \left(S_{in} + \Delta S_{QD} \right)}{T_s S_{in}} \right] \tag{5}$$

underscoring that decoherence actually lowers the thermodynamic efficiency limit of the PV cell.

In summary, the limitations of Scully's hypothesis for increased power conversion efficiency (i.e. higher voltage) from a semiconducting *p-i-n* junction PV cell utilizing quantum coherence in the intrinsic quantum dots were discussed above. One known way of generating higher voltage from a PV cell, the end goal of Scully's quantum coherent approach, is to use more than one *p-n* junction subcell to form a multijunction PV cell as initially proposed by Jackson [11] capable of utilizing the incoherent polychromatic solar spectrum much more efficiently. In fact, this has been realized with impressive power conversion efficiency levels in series-connected, monolithic triple junction PV cells comprised of, for example, a GaInP top subcell, a GaInAs middle subcell, and a Ge bottom subcell [12]. Moreover, there remains ample opportunity for further improvement in multijunction PV cells including optimizing minority carrier lifetime through careful device design, use of thinner subcells, improved spectrum matching, better photon management (e.g. through improved broadband anti-reflection coatings), and finding ways to reduce series resistance and I^2R loss.

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Corresponding author e-mail address: apkirk@utdallas.edu

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