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Observation of Reciprocity between Photovoltaic External Quantum Efficiency and Radiative Luminescence in III-V Nanostructured Solar Cells

Roger E. Welser and Ashok K. Sood
Magnolia Optical Technologies, Inc.
52-B Cummings Park, Suite 314, Woburn, MA

Nibir K. Dhar
Night Vision & Electronics Sensors Directorate,
10221 Burbeck Road, Fort Belvoir, VA 22060

Priyalal S. Wijewarnasuriya
Army Research Laboratory,
2800 Powder Mill Road, Adelphi, MD 20783

Abstract

The reciprocity between photovoltaic external quantum efficiency and radiative luminescence in a variety of reported nanostructured III-V quantum well and quantum dot solar cell devices is examined. In some device structures, the emission spectrum calculated from the measured external quantum efficiency closely matches the measured luminescent spectrum. However, in other devices, significant offsets between the calculated and measured emission spectrums are observed, perhaps due to non-isotropic emissions. Reciprocity relations can also be used to calculate the radiative dark current in specific devices using the measured photovoltaic external quantum efficiency. While many quantum well and quantum dot devices are limited by non-radiative recombination, a few select devices are approaching the radiative limit of operation and thus could benefit from novel structures which inhibit radiative recombination.

INTRODUCTION

The concept of detailed balance between optical absorption and emission is often used to estimate the limiting efficiency of ideal photovoltaic devices. Since its introduction by Shockley-Queisser, detailed balance calculations have been generalized to include a continuous absorbance function and a variety of different cell geometries [1-3]. More recently, detailed balance concepts have been further generalized and applied to the analysis of experimental results from several different types of functional photovoltaic devices [4-6]. In this paper, we employ generalized detailed balance principles to the analysis of quantum well and quantum dot solar cells.

Nanostructured quantum well and quantum dot solar cells are being widely investigated as a means of extending infrared absorption for better current matching in multi-junction III-V cells and as a means to implement advanced device designs which promise to break traditional limits on photovoltaic performance. In this work, we examine the reciprocity between photovoltaic external quantum efficiency and radiative emissions in several different reported quantum dot and quantum well device structures. Of particular note is the behavior of multi-step well structures, which exhibit performance characteristics consistent with inhibited radiative recombination. Inhibited radiative recombination could improve the efficiency of photovoltaic devices if non-radiative recombination is also sufficiently suppressed.

RECIPROCITY BETWEEN EQE AND LUMINESCENCE

In recent years, Uwe Rau [4] and others have explored anew the reciprocity between light collecting PV devices and light generating LED devices. In general, detailed balance concepts can be used to relate radiative emissions from a semiconductor device to the product of the photovoltaic external quantum efficiency and the equilibrium black body radiation. In general, the radiative luminescence spectrum, $L_{rad}(E)$ can be expressed by the following relation:

$$L_{rad}(E) = C(E) * EQE(E) * BB(E) \qquad (1)$$

where EQE (E) is the measured EQE spectrum, BB (E) is the equilibrium blackbody spectrum with refractive index n=1, and C (E) is the appropriate scaling factor. When the radiative emissions are driven by an applied voltage (e.g. electroluminescence), C (E) will increase exponentially with the applied voltage. When the radiative emissions are enhanced by optical pumping (e.g. photoluminescence), C (E) will increase the pump intensity. In both cases, C (E) will also include factors which account for both measurement specifics and various loss mechanisms, including measurement-related collection losses and device-specific optical losses and non-isotropic emissions. In this work, we apply this general reciprocity relation summarized in Equation (1) to analyze reported results from relevant nanostructured quantum well and quantum dot devices.

Our initial analysis considers the reported electroluminescence (EL) and external quantum efficiency (EQE) spectra from a strain-balanced multiple quantum well structure developed by a group led by the Imperial College London [7]. This structure employs relatively thick, approximately 10.5 nm InGaAs quantum wells. As seen in Figure 1, there is an excellent agreement between the measured EL spectrum and the EL spectrum calculated from Equation (1) using the measured EQE spectrum. In this calculation, C (E) was assumed to be independent of energy (E).

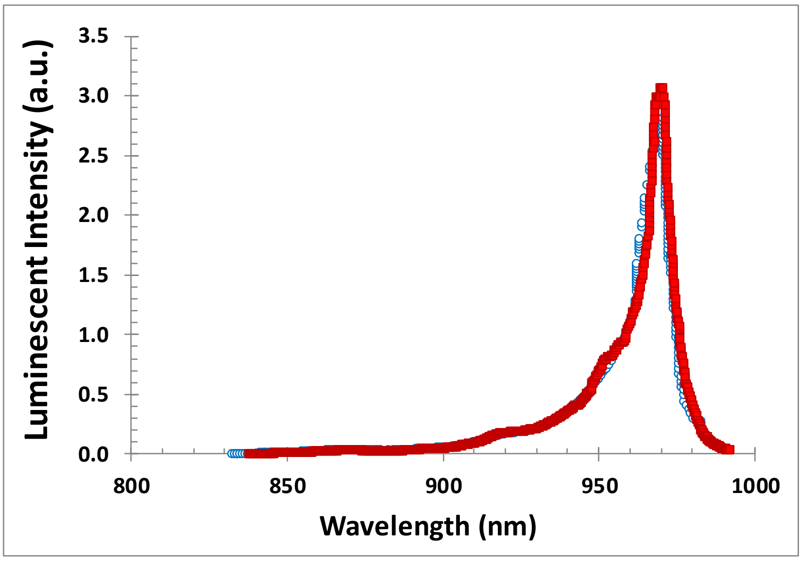

Figure 1: Comparison of the measured luminescence spectra (solid red squares) to the luminescence spectra calculated from the measured EQE spectra (open blue circles) from a multiple quantum well structure [7].

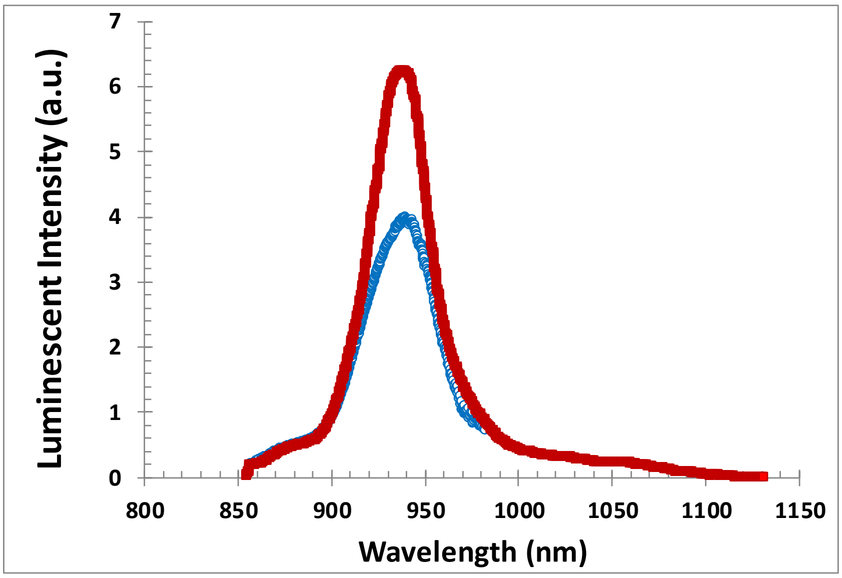

Figure 2: Comparison of the measured luminescent spectra (solid red squares) to the luminescent spectra calculated from the measured EQE spectra (open blue circles) from a quantum dot superlattice structure [8].

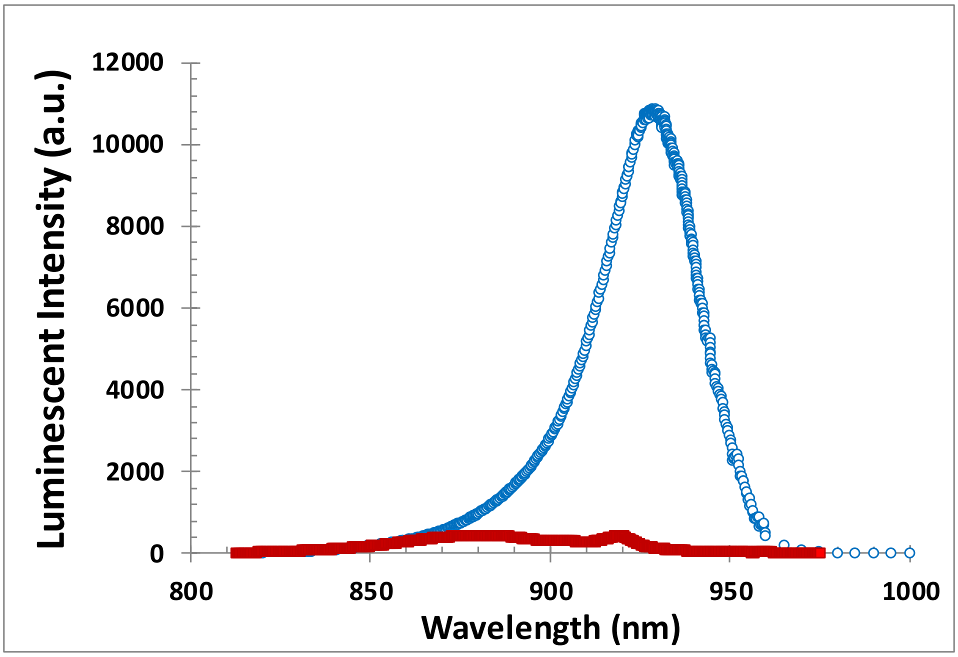

Figure 3: Comparison of the measured luminescent spectra (solid red squares) to the luminescent spectra calculated from the measured EQE spectra (open blue circles) from a multi-step quantum well superlattice structure [13].

Figure 2 compares the measured and calculated EL spectra from a strain-balanced quantum dot structure reported by a group at RIT [8]. In this case, the measured peak EL intensity is roughly 1.5x higher than the EL calculated from the EQE. The peak emission in this QD structure is not from the dots, but from the wetting layers, which effectively forms a thin InAs QW. Thin QWs will force a tighter overlap of the electron and hole wave functions, and have been observed to enhance luminescence. In Figure 2, a better fit could be obtained by using a higher C (E) to describe well emissions than bulk GaAs emissions.

While a thin QW can lead to an increase in wave function overlap, some structures can result in a reduction in wave function overlap [9-12]. Figure 3 compares the measured and calculated EL spectra from a strain-balanced quantum well superlattice structured reported by a group at the University of Tokyo [13]. In this structure, a multi-step well profile is employed, and the calculated peak EL intensity is over an order of magnitude higher than the measured EL spectrum. In Figure 3, a better fit could be obtained by using a lower C (E) to describe well emissions than bulk GaAs emissions.

CALCULATION OF RADIATIVE DARK CURRENT

The reciprocity relation summarized in Equation (1) can also be used to calculate the radiative dark diode current of a device from its measured photovoltaic external quantum efficiency. In general, the radiative dark diode current (J_{rad}) can be found by integrating the luminescent spectrum – Equation (1) – over energy and over the angle of emission. Assuming that EQE (E) is the measured EQE spectrum at normal incidence, BB (E) is the equilibrium blackbody spectrum with refractive index n=1, and β (V) is the standard exponential n=1 voltage dependence of a diode, then

$$J_{rad}\,(E) = q\,F_{dc}\,\beta\,(V) \int EQE\,(E)\,BB\,(E)\,dE \qquad (2)$$

where F_{dc} is a dark diode current factor that takes into account the specific refractive index medium in which the absorber layers are embedded and any resulting non-isotropic absorption and emissions. If the absorber layers are sufficiently thin and are surrounded by cladding layer with refractive index n_b, then $F_{dc} = 2\pi n_b^2$ [14]. On the other hand, any reabsorption of emitted photons (e.g. photon recycling) or other restrictions in the angle of emission resulting in non-isotropic emissions will lower F_{dc} and thus effectively inhibit radiative recombination.

Figure 4 compares the radiative dark diode current calculated from Equation (2) and assuming $n_b = 3.5$, using the measured external quantum efficiency from two reported quantum dot solar cell (QDSC) structures [8,15]. Figure 4 also compares the shifted IV curve of the two reported QDSC structures [1]. The shifted IV curves are derived from the measured illuminated IV curves minus the short circuit current [16]. Although series resistance effects will cause the shifted IV curves to overestimate the diode dark current, these curves nevertheless provide both absolute and relative information about the underlying diode characteristics.

The shifted IV characteristics suggest that the dark diode current in both devices is largely dominated by an n=2 component, presumably non-radiative recombination within the diode junction depletion region. However, the n=2 space charge recombination is many orders of magnitude higher in the device from the Universidad Politécnica de Madrid (UPM). Comparison of the shifted IV characteristics to the calculated radiative dark current in Figure 4 suggests that while radiative recombination does not play any role in limiting the performance of the QDSC device reported by UPM, radiative recombination may be playing a small role in the QDSC device reported by RIT.

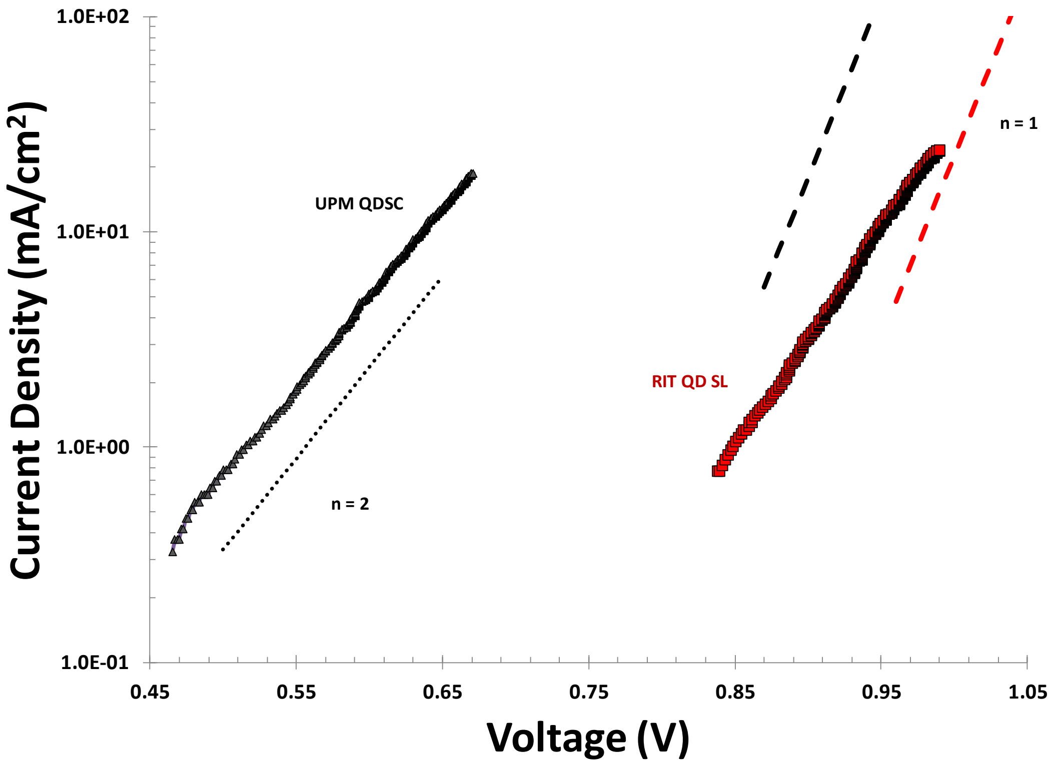

Figure 4: Comparison of the shifted illuminated current-voltage (IV) characteristics from two quantum dot solar cell structures reported by groups at the Universidad Politécnica de Madrid (UPM) the Rochester Institute of Technology (RIT) [8,15]. Also shown are the estimated n=2 space charge recombination and the calculated n=1 radiative current components.

A group led by Imperial College London has reported signs of radiative recombination limiting the voltage output of their multiple quantum well (MQW) solar cell devices, but only at higher concentration levels [17]. As can be seen in Figure 5, their devices are dominated by n=2 space charge recombination at one-sun illumination levels. However, comparison of the shifted IV characteristics to the calculated radiative dark current using Equation (2) suggests that the Imperial device may be somewhat limited by radiative recombination at high bias levels as reported.

Figure 5 also compares the shifted current-voltage characteristics and calculated radiative current from a high-voltage MQW device developed by Magnolia. In this device, the n=2 space charge recombination component has been significantly reduced, better exposing the limiting n=1 diode component. This Device appears to be reaching the radiative limit of operation at one-sun illumination levels. Higher efficiency could be realized in this low dark current device if the radiative recombination rate can be suppressed, for example by restricting the angle of emission or enhancing hot carrier extraction [20].

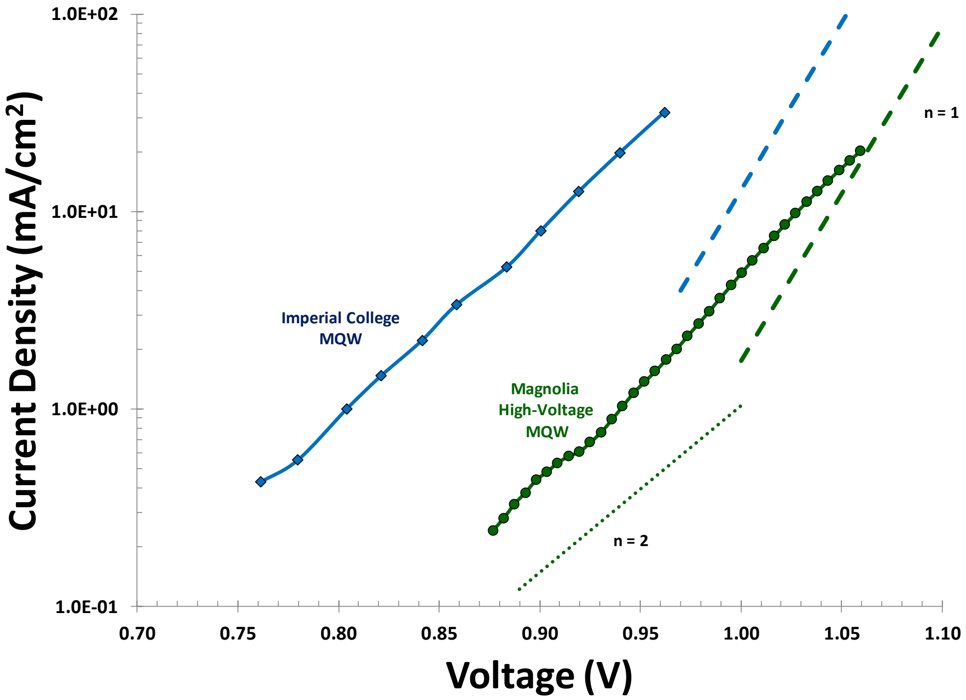

Figure 5: Comparison of the shifted illuminated current-voltage (IV) characteristics from two multiple quantum well (MQW) solar cell structures reported by groups at the Imperial College London and Magnolia [18-19]. Also shown are the estimated n=2 space charge recombination and the calculated n=1 radiative current components.

CONCLUSIONS

While much of the past work in the field of III-V nanostructured quantum well and quantum dot solar cells has unfortunately been marred by high non-radiative recombination rates and low operating voltages, a few select devices appear to be reaching the radiative limit of operation. To first order, the role of radiative recombination in a specific device can be assessed by comparing the measured luminescent spectrum to the spectrum calculated from the measured photovoltaic external quantum efficiency. In devices employing a step-graded well profile significant offsets between calculated and measured emission spectrums are observed, consistent with inhibited radiative recombination.

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