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Investigation and modeling of photocurrent collection process in multiple quantum well solar cells

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ABSTRACT

Solar cells employing quantum wells can enhance the light absorption but suffer from the difficulty in photocarrier extraction. Here, we analyzed the spectral response and the photocarrier collection mechanism of p-i-n multiple quantum well (MQW) solar cells using the effective-mobility model. Both the simulation and experimental results imply that the spatial profiles of electron and hole densities in MQWs play an important role in the carrier collection process. By considering the recombination increment under illumination, our findings suggest that the concept of the majority/minority carriers is important even in the intrinsic region: photogenerated electrons and holes only experience significant recombination when passing through the hole-rich and electron-rich regions, respectively. This can accurately explain the photocurrent behavior in cells with background doping, background illumination, and different MQW positions. Based on the experimental findings, we derived analytical formulae for carrier collection efficiency, which directly show the impact of each cell parameter and can be used for the systematic cell design.

1. Introduction

The implementation of nanostructures such as multiple quantum wells (MQW) in the photovoltaic application has been proposed as a promising approach for the efficient conversion of the sunlight spectrum into the electrical energy [1]. Such structures allow us to modify the optical properties in order to enhance the solar cell performance. A wide range of application of MQW solar cells, such as the photocurrent enhancement with small voltage loss [2], the restriction of radiative recombination [3], and the utilization of excitonic absorption [4], have been investigated. Another potential application which has already been commercially realized [5] is the bandgap engineering of subcells in multi-junction solar cells [3,6–9], where the bandgap combination is vital to the cell performance. MQW structures reduce the effective bandgap while keeping effectively lattice-matched with the substrate, offering alternative material choices for the bandgap optimization in multi-junction cells.

However, MQW absorbers have difficulty in carrier collection due to the obstruction of carrier transport by potential barriers [10]. Photogenerated carriers which are trapped and cannot escape out of the MQWs recombine and do not contribute to the photocurrent. MQWs are usually inserted in the intrinsic regions of the p-i-n junctions, where the internal electric field can enhance the carrier extraction [11]. Still, poor carrier collection has been observed in MQWs that have a large number of stacks and/or large band offsets [9,11–13].

To deal with this problem, there are a number of research works studying the mechanisms of carrier escape from the quantum wells (QWs). Escape models, such as thermal escape and tunnel escape, have been proposed, and detailed calculations of their escape rates have been discussed analytically [14,15]. However, a theoretical model which links the carrier escape (microscopic behavior) with the output photocurrent (macroscopic behavior) has not been well established. This limits the investigation of the device operation to the self-consistent numerical simulation [16], which is not straightforward to understand the device behavior. In addition, the numerical simulator is not always convenient to see the impact of cell parameters and optimize the cell design. Various analytical expressions have been employed to describe the collection efficiency of the charge carriers from MQWs such as $(1/\tau_{esc})/(1/\tau_{esc} + 1/\tau_{rec})$, $[(1/\tau_{esc})/(1/\tau_{esc} + 1/\tau_{rec})]^N$, and $(N/\tau_{esc})/(N/\tau_{esc} + 1/\tau_{rec})$, where τ_{esc} is the carrier escape time from a QW to the next QW through a barrier, τ_{rec} is the recombination lifetime, and N is the stack number of QWs [12,13,17,18]. In addition to a variety of

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expressions, they are over-simplified. They do not take into account the backward movement of carriers, the driving force from the electric field, and the carrier distribution. Note that the above collection-efficiency expressions have only a weak dependence on the internal field,[1] contradicting the fact that the internal field of the p-i-n structure is essential for the carrier collection from the MQW.

Many experimental studies have reported that the carrier collection from the quantum structures strongly depends on the surrounding conditions. It is well recognized that unintentional background doping extensively affects carrier collection [19–21]. This has been attributed to the weak electric field caused by band flattening, but only the band flattening cannot describe all the behaviors, which will be mentioned in this paper. The background illumination (bias light) has been reported to change the collection efficiency of the photoexcited carriers [22], but the mechanism behind this phenomenon has not been well-understood.

Here, we investigate the photocurrent collection mechanism, particularly the role of carrier distribution, in MQW solar cells. We employ the effective-mobility model, which takes into account the random carrier motion and the electric field, to simulate and analyze the results. Based on our experimental findings on various measurement conditions, we propose explicit expressions for carrier collection efficiency, which provides design rules for efficient photocarrier collection.

2. Experimental and simulation details

2.1. Sample preparation

The p-i-n solar cells in this study were prepared by metal-organic vapor phase epitaxy with the growth condition explained in [21]. The thicknesses of the 2×10^{18} cm^{-3} doped GaAs p-emitter and the 1×10^{17} cm^{-3} doped GaAs n-base were both 200 nm. We applied a 25-nm InGaP window, but did not apply a back surface field and an anti-reflection coating. $\mathrm{In_{0.20}Ga_{0.80}As}$ (5.4 nm)/$\mathrm{GaAs_{0.61}P_{0.39}}$ (5.7 nm) strain-balanced MQWs were inserted in the i-regions, whose thickness was kept constant at 1100 nm for all samples. The atomic compositions and thicknesses of the MQWs were confirmed by X-ray diffraction (XRD) measurements.

We prepared two sets of samples as summarized in Table 1. The first set consisted of three MQW cells with different background doping levels in the i-regions. For convenience, we call them i-regions regardless of the background doping. The i-region of the p(p)n cell was unintentionally p-doped by carbon during the growth process, whereas the i-regions of the pin and p(n)n cells were additionally doped by small supply rates of H_2S. The background doping levels, shown in Table 1, were confirmed by Hall measurements in the GaAs test samples grown in the same condition. The second set consisted of cells with MQWs inserted in different positions in the i-regions: near the emitter (MQW-top), at the center (MQW-mid), and near the base (MQW-bottom). In this sample set, the compensation doping in the i-regions was carefully applied to guarantee the uniform electric field inside the MQWs. Samples within the same set were grown in the same batch and confirmed by XRD measurement to assure the identical structure of the MQWs.

Table 1
Sample details.

Sample	Well number	i-GaAs spacer [nm]		Background doping [cm^{-3}][c]
		Emitter side	Base side	
p(p)n	45[a]	300	300	p-type 3×10^{15}
pin	45	300	300	n-type 5×10^{14}
p(n)n	45	300	300	n-type 8×10^{15}
MQW-top	27[b]	100	700	$< 5 \times 10^{14}$
MQW-mid	27	400	400	$< 5 \times 10^{14}$
MQW-bottom	27	700	100	$< 5 \times 10^{14}$

[a] The total MQW thickness was 500 nm.
[b] The total MQW thickness was 300 nm.
[c] Obtained from Hall measurements in GaAs test samples.

2.2. Carrier collection efficiency (CCE) measurement

Since most photogenerated carriers can be collected from the MQW under sufficient reverse bias owing to high electric field, carrier collection efficiency (CCE) can be estimated by normalizing the current as

$$\mathrm{CCE}(V) = \Delta J(V)/\Delta J(V_{\mathrm{reverse}}), \tag{1}$$

where ΔJ is the current increment after illumination, which corresponds to the *photocurrent*, V is the voltage, V_{reverse} is the sufficiently high reverse-bias voltage [22]. For the illumination with monochromatic light having wavelength λ, Eq. (1) can also be written using external quantum efficiency (EQE) as

$$\mathrm{CCE}(V, \lambda) = \mathrm{EQE}(V, \lambda)/\mathrm{EQE}(V_{\mathrm{reverse}}, \lambda). \tag{2}$$

CCE excludes the parasitic absorption (e.g. substrate absorption, which is included in the internal quantum efficiency measurement) and is straightforward in evaluating the collection process involving MQWs, but the careful interpretation is needed near the band edge, where the quantum-confined Stark effect arises.

EQE was measured using monochromatic light with a constant intensity of 2.5 mW/cm^2 passing through a chopper with a frequency of 85 Hz and captured by a lock-in amplifier, whose phase was carefully corrected. In the study of the light bias, additional AM1.5G light with an intensity of 100 mW/cm^2 (1 sun) was illuminated as a background without passing through the chopper. We focused on an operation voltage of 0.6 V, where the carrier transport degradation can be clearly observed while the effects from a voltage drop across the parasitic resistance [22] is sufficiently small. V_{reverse} was set to -6 V in the CCE measurement.

2.3. Simulation and effective-mobility model

The experimental results were analyzed using the device simulator (PVcell, STR) [23]. The simulation was based on the conventional drift-diffusion model, solving the current continuity and Poisson's equations without additional complex physics. The Shockley-Read-Hall (SRH) recombination rate through deep-level defects formulated as

$$R_{\mathrm{SRH}} \approx \frac{np}{\tau_p n + \tau_n p} \tag{3}$$

was included in the current continuity equation. Here, τ_n and τ_p are the electron and hole SRH lifetimes, and n and p are the electron and hole densities. The illumination intensity, the applied voltage, the surface reflectance, and the device structure were set to be the same as the experimental condition except for the MQW structure.

To reduce the complexity of the MQW while maintaining its essence, we employed the effective-mobility model [24,25] in the device simulation. Instead of the periodic potential profile of wells and barriers, the MQW region is approximated as an equivalent bulk with a low effective mobility representing the sequential carrier trap-and-escape transport. We obtained the effective mobilities experimentally from the carrier time-of-flight measurement [26], which accidentally had similar values for electrons and holes [27]. The background doping level in the equivalent bulk was assumed to be approximately half of the value measured in GaAs, as the dopant ionization energy in wide-gap materials is relatively large [28] and the wide-gap GaAsP occupied

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[1] For instance, the thermal escape rate from a QW with width w and effective height V_b under the electric field E to the next well is proportional to $\exp\left[-\left(V_b - \frac{1}{2}wE\right)/k_B T\right]$ [14]. For $w = 5$ nm, the escape rate is boosted by less than 10% under $E = 10$ kV/cm compared to that under flat-band.