Improved performance of In(Ga)As/GaAs quantum dot solar cells via light scattering by nanoparticles

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(Received 12 June 2009; accepted 31 July 2009; published online 9 September 2009)

InAs quantum dots have been used to extend the absorption edge of InGaAs/GaAs quantum well solar cells from 940 to ~1100 nm. In order to improve absorption of infrared radiation by the thin (300 nm) active layer, we exploit its high refractive index, which acts as a waveguide for certain frequencies of light. Surface-deposited nanoparticles scatter incident radiation into waveguide modes of the devices, yielding improved infrared photocurrent generation of at least 10% at all wavelengths between 700 and 1100 nm, short-circuit current density increases of up to 16%, and corresponding gains in power conversion efficiency. © 2009 American Institute of Physics. [doi:10.1063/1.3213366]

Solar cells based on low-dimensional semiconductor structures are currently of outstanding interest for development of high-efficiency photovoltaics.¹⁻⁴ In particular, quantum well solar cells (QWSCs) and quantum dot solar cells (QDSCs) have been proposed as a means of exceeding the Shockley–Queisser limit of ~31% power conversion efficiency for homojunction devices.¹⁻⁵ Incorporation of QDs in the context of our work is attractive for achieving long wavelength absorption in solar cells because they are not limited by selection rules for optical transitions in QWs and because their size helps to mitigate strain effects in the active layer. While QDs have been proposed for use in a variety of photovoltaic concepts, such as the intermediate band solar cell⁵ and multiexciton generation devices,⁷ they serve here to extend the absorption of QW-based devices to longer infrared wavelengths that are essential for realizing high efficiency, while maintaining the waveguiding characteristics of QWSCs⁸ to enhance infrared photocurrent generation, including at wavelengths that are absorbed exclusively by QDs. Here, we present results of photocurrent and short-circuit current density enhancement in In(Ga)As/GaAs QDSCs via scattering of light by metal and dielectric nanoparticles into optical waveguide modes of the QD device structure and demonstrate that coupling of radiation into those modes can produce enhancement at all infrared wavelengths in the device photocurrent spectrum.

Epitaxial layer structures, shown schematically in Fig. 1(a), were prepared by molecular beam epitaxy on 2 in. n⁺-GaAs (001) substrates on which a buffer layer of 200 nm n⁺-GaAs was grown first. The active regions of the QDSCs nominally consist of ~300 nm of intrinsic material: specifically, 10 iterations of the sequence (22 nm GaAs, 4 nm In₀.₁₁Ga₀.₈₉As, 2.6 ML InAs, 4 nm In₀.₁₁Ga₀.₈₉As). The InAs was annealed at 500 °C to form QDs, as described in detail elsewhere.⁹ The QD structures exhibit a room temperature photoluminescence peak wavelength of 1175 nm with a full width at half maximum of 100 nm. Atomic force microscopy (AFM) topographs (not shown) show no evidence of cross hatching on the wafer surface, implying that strain relaxation and formation of misfit dislocations are negligible. Reference devices with 300 nm of either intrinsic GaAs or 8 nm In₀.₁₁Ga₀.₈₉As QWs (no QDs) with 22 nm GaAs barriers were also grown. The n⁺-GaAs bottom contact metallization…

FIG. 1. (a) Schematic of the device structures of QD- and QWSCs employed in this study. (b) Scanning electron micrographs of typical deposition results for AuNPs (left) and SNPs (right), with concentrations of ~5 × 10⁶ cm⁻² and ~2.5 × 10⁶ cm⁻², respectively.

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0021-8979/2009/106(5)/056101/3/$25.00 106, 056101-1 © 2009 American Institute of Physics

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consisted of 20 nm Pd/40 nm Ge/40 nm Ti/50 nm Au and the p⁺-GaAs contact consisted of 100 nm Pd. All metals were deposited by electron beam evaporation. Photolithography and a standard lift-off procedure were used to fabricate windows in the top contact and to enable sputter deposition of a 15 nm thick SiO₂ passivation layer on the windows of the solar cells.

Devices were evaluated at room temperature in terms of their zero-bias photocurrent response (Iₚᵦ) and illuminated current density versus voltage (J-V) characteristics, both with and without nanoparticles deposited on the top surface. Photocurrent measurements were performed using a custom monochromator system and illuminated J-V measurements were taken using normally incident light from a Newport Oriel 96000 solar simulator operating at 150 W with an air-mass (AM) 1.5 global filter. In this study, we used 100 nm diameter Au (AuNP) or 150 nm diameter SiO₂ (SNP) colloidal particles from nanoComposix, Inc., which were deposited in a humid environment for 30–60 min from solutions containing between 1 x 10¹⁰ and 4 x 10¹² ml⁻¹ onto devices pretreated with poly-L-lysine. Scanning electron micrographs of AuNPs and SNPs deposited at typical concentrations of ~5 x 10⁶ and ~2.5 x 10⁹ cm⁻², respectively, are shown in Fig. 1(b). Both types of particles scatter light strongly but they exhibit different wavelength-dependent behavior: AuNPs, around 500 nm (near the surface plasmon polariton resonance), destructive interference between the scattered and incident fields reduces the magnitude of the transmitted field. This loss mechanism, which is associated with a dipolar mode of the AuNPs, is insignificant for SNPs at the wavelengths of interest. Clusters of metal particles also reduce the transmitted field amplitude by reducing scattering compared to individual particles, while the effects of dielectric particle clustering are much less severe.

Photocurrent response spectra were measured and used to calculate internal quantum efficiency (IQE), shown in Fig. 2(a). These results confirm that the addition of QDs enables additional carrier generation and collection at infrared wavelengths. A calibrated Newport 818UV photodiode was measured under the same conditions as our test devices, and calculated surface reflection losses were subtracted in order to estimate IQE. From our photocurrent measurements, we see that the GaAs cell and QWSC cut off abruptly at 890 and 940 nm, respectively. The photocurrent response of the QDSC extends well above its peak for QD absorption at 980 nm, reaching zero at 1150 nm. We attribute the tail in the QDSC spectrum to inhomogeneous broadening of QD absorption associated with variations in dot sizes. Devices fabricated from different parts of the same wafer varied in performance by up to 6%, which is within the order of variation over a wafer with epitaxial growth, so differences in IQE between 400 and 850 nm should be negligible. We also note that the IQE of QDSCs above 850 nm is not degraded compared to QWSCs, indicating negligible effects of photocarrier trapping due to the addition of QDs.

Following nanoparticle deposition, improvements in short-circuit current density (Jₛₑ) were observed in QDSCs. Figure 2(b) shows current density (J) versus voltage for QDSCs, where calculation of J used unmetallized device area.

We note that Jₛₑ in our devices is somewhat lower than typically reported values for high efficiency cells, as our QDSCs have not been fully optimized for photovoltaic performance and our experimental conditions correspond to lower illumination intensity than standard AM 1.5 conditions. Using SNPs and AuNPs, respective Jₛₑ increases of 16% and 3% have been achieved for QDSCs relative to devices with no nanoparticles. Open-circuit voltages and fill factors exhibited negligible changes following particle deposition, so Jₛₑ enhancements correspond to equal improvement factors in cell efficiencies.

Finite-element electromagnetic simulations using COMSOL software were performed in three dimensions to analyze the mechanisms of enhancement in our devices. In the simulations, the integrated magnitude-squared of the electric field in the semiconductor volume, |E|², was computed as a function of wavelength for devices with and without nanoparticles on the surface to obtain Gnp and Gbare, respectively. These quantities are expected to be proportional to optical transition rates and, consequently, to photocurrent generation for unity carrier collection efficiency. Figures 3(a) and 3(b) show Gnp/Gbare, which we take as an estimate of the expected photocurrent enhancement in QDSCs due to the presence of AuNPs and SNPs. With regard to the simulations, we see that photocurrent enhancement is generally expected in the range of 500–1100 nm for AuNPs and 400–1100 nm for SNPs. These improvements result from forward scattering of incident electromagnetic radiation by the nanoparticles, which increases light transmission through the air-semiconductor interface compared to a bare device.

For both AuNPs and SNPs, the measured photocurrent enhancement was typically greater than these simulations predicted. Specifically, the experimental spectra show additional broad enhancements in photocurrent due to light cou-
Radiation modes, for which photons can undergo multiple
propagating into waveguide modes, including substantial improvements at infrared wavelengths. In most cases where the simulations underestimate enhancement, it is because the simulation volume supports an insufficient number of waveguide modes for their effects to be seen. The actual device structures, however, support many optical modes. Following the analysis of Soller and Hall,\textsuperscript{12} calculations indicate that radiation from a horizontal electric dipole atop our structures (serving as a proxy for a nanoparticle excited by incident electromagnetic radiation) couples into two types of evanescent modes: guided modes, which are evanescent outside the guiding layer, and substrate radiation modes, which are evanescent in the source region (air/dielectric) but propagate in the device substrate. Using the method of Ref. 12, we calculated $\mathcal{S}(\nu)$, the power spectrum for dipole emission into our device structure, for wavelengths between 400 and 1100 nm and found that over 80\% of scattered light enters substrate radiation modes, for which photons can undergo multiple internal reflections, substantially increasing the likelihood of absorption. With the majority of light entering substrate radiation modes, this effect is primarily responsible for the observed $I_{\text{ph}}$ enhancements. Secondary gains result from light below 900 nm coupling weakly into true guided modes but with a peak efficiency of $\sim$10\% due to the small difference between the refractive indices of InGaAs and GaAs. Since our finite-element simulations do not capture the effects of waveguiding, the differences between them and our experiments highlight the benefit of optical waveguiding for QDSCs.

Experimental results also reveal substantial enhancement at short wavelengths, as seen in Fig. 3(b), where there is a prominent increase in photocurrent of $\sim$50\% at 400 nm in the experimental data that are not predicted by modeling with SNPs. Interestingly, the simulation of a randomly textured SiO$_2$ surface with 150 nm tall features qualitatively predicts the experimental result more accurately than the nanoparticle simulation. This is because the deposited SNPs, which are densely clustered, produce characteristics more akin to a rough film than to individual particles. The similarity is not unexpected, as surface texture scattering is a well-known method for increasing transmission of light,\textsuperscript{13,14} and nanoparticles perform the same function. SNPs are not a homogeneous film, however; their antireflective behavior is weaker than that of a true thin film and it is ultimately of secondary importance to the $J_{\text{ph}}$ and $J_{\text{sc}}$ enhancements observed. The scattering provided by the nanoparticles is essential for coupling light into waveguide modes, and, indeed, the most significant benefit of SNPs is photocurrent enhancement of 10\%–20\% due to partial trapping of light between 500 and 1100 nm in substrate radiation modes.

In summary, we have demonstrated that QD structures are effective in extending the photocurrent response of QWSCs to wavelengths well beyond the QW absorption edge and we show that optical scattering from nanoparticles can substantially enhance the performance of QDSCs by coupling light into waveguide modes of the QD structure. Photocurrent at infrared wavelengths increased by $\sim$10\% following deposition of SiO$_2$ nanoparticles relative to the bare devices, resulting in an enhancement factor of over 15\% in short-circuit current density and power conversion efficiency. It is encouraging to note that these improvements were achieved even though $\sim$80\% of scattered light entered substrate radiation modes. This suggests that even greater enhancement should be possible with a better waveguide structure, which could help QDSCs to become very high-efficiency devices.

The authors would like to thank Jeremy Law (UCSD) for assistance with AFM scans and useful discussion, Peter Matheu (UC Berkeley) for advice on nanoparticle deposition and Thomas Darlington (nanoComposix, Inc.) for assistance with obtaining nanoparticles. Part of this work was supported by NSF (Grant No. DMR 0806755) and DoE (Grant No. DE-FG36086018016).

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