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High-efficiency InAs/GaAs quantum dot solar cells by metalorganic chemical vapor deposition

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We fabricate a high-efficiency InAs/GaAs quantum dot (QD) solar cell. It contains five layers of high-density self-assembled InAs QDs grown by metalorganic chemical vapor deposition suppressing open-circuit-voltage (V_{OC}) degradation. We develop a dual-layer anti-reflection coating of optimum thicknesses. The resulting cell exhibits efficiencies of 18.7% under AM1.5 G for 1 sun and 19.4% for 2 suns. Concentrator measurements demonstrate the advantage of QD use under concentrated illumination, owing to the significant increase in V_{OC}. We also find a V_{OC} offset of 0.3 V from the QD ground-state transition energies for QD cells, in contrast to 0.4 V for state-of-the-art bulk semiconductor cells. [http://dx.doi.org/10.1063/1.4714767]

Semiconductor QD solar cells are theoretically predicted to achieve ultrahigh-efficiency solar-energy conversion in single *p-n* junction structures by utilizing intermediate-level energy bands.[1–3] Among the wide range of semiconductor materials for QD solar cells currently under intensive study,[4–6] those using III-V semiconductor compound InAs/GaAs QDs (i.e., InAs QDs embedded in GaAs matrices) have exhibited the highest efficiencies and robustness.[7–9] However, so far most experimental studies for such solid-state QD cells unfortunately have resulted in lower efficiencies by incorporation of QDs presumably mainly due to QD interfacial carrier recombination, which severely reduces open-circuit voltage (V_{OC}). For this reason, most reported efficiencies of QD solar cells have been significantly lower than those of the best single-junction cells without QD.

We previously demonstrated that we could suppress the V_{OC} degradation in incorporation of QDs into GaAs solar cells grown by metalorganic chemical vapor deposition (MOCVD).[10] Taking advantage of this reduced-V_{OC}-degradation scheme, we demonstrate high efficiency InAs/GaAs QD solar cells in conjunction with a development of anti-reflection coating in this present work.

The InAs/GaAs QD solar cell we fabricated has a *p-i-n* GaAs structure with a 300-nm-thick *i*-GaAs layer embedding five layers of self-assembled InAs QDs with a density of 4×10^{10} cm^{-2} per layer. The cell structure was grown on an *n*-GaAs (100) substrate by MOCVD. Our solar cell devices are 4×4 mm^2 area cleaved pieces. A part of the front and the entire back surfaces were metalized with Au/AuGeNi and Au/Cr, respectively, by electron-beam evaporation. The nonmetalized part of the top p^+-GaAs contact layer was removed at room temperature by selective chemical etching with 50% citric acid/H_2O_2 (4:1 vol./vol.). The room-temperature photoluminescence spectrum from the QD cell exhibits a peak associated with the ground-state emission of the InAs QDs at 1.0 μm with a full-width at half-maximum of 65 meV. This QD cell corresponds to *QDSC-3* in Ref. 10.

In this work, we have applied an antireflection coating with MgF_2/ZnS on the front surface of the cells with an optimized set of layer thicknesses (100-nm MgF_2/50-nm ZnS). These thicknesses were chosen through one-dimensional electromagnetic calculations for reflectivities, shown in Figure 1, based on the *Rigorous Coupled Wave Analysis*. At the time of our work cited in Ref. 10, we had no standard solar-simulator light source and, therefore, instead used a halogen lamp with ~1 sun intensity calibrated indirectly with a reference GaAs cell whose photocurrent value had been known under AM1.5 G, 1 sun illumination. Because of the indirect calibration, the light current-voltage (*I-V*) characteristics of the QD cells measured for Ref. 10 were slightly different from those under the standard 1-sun solar spectrum. In this present work, we used a calibrated AM1.5 G solar simulator for light *I-V* measurements.

Figure 2 shows the light *I-V* characteristics of the InAs/GaAs QD cell under AM1.5 G, 1-sun (100 mW cm^{-2}) illumination. The device performance parameters were as follows: short-circuit current $J_{SC} = 26.0$ mA cm^{-2}, $V_{OC} = 0.90$ V, fill factor $FF = 0.80$, and energy conversion efficiency $\eta = 18.7\%$. In addition, 19.4% efficiency was observed for 2 suns (200.9 mW cm^{-2} illumination, $J_{SC} = 54.2$ mA cm^{-2},

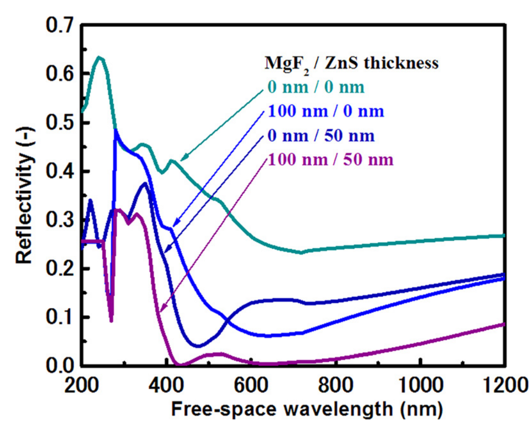

FIG. 1. Calculated reflectivities of GaAs solar cell front surfaces with varied coating material thicknesses.

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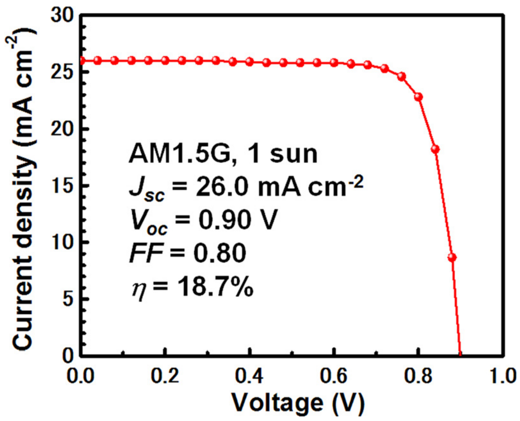

FIG. 2. Light *I-V* characteristics of the fabricated InAs/GaAs QD solar cell under AM1.5 G, 1 sun illumination.

$V_{OC} = 0.93$ V, and $FF = 0.77$). Achieving such a high efficiency in a cell grown by MOCVD, which is suitable for mass production, is strong motivation for future commercialization of high-efficiency QD solar cells.

Figure 3 shows the dependence of V_{OC} on the illumination intensity in suns for the high-efficiency QD cell (5-layer 1.0 μm InAs QDs, 11-nm-thick spacer layers (SLs)) described above, a QD cell with thicker SLs (5-layer 1.1 μm QDs, 40 nm SLs), and a cell with only wetting layers (WLs) (no QD, 5-layer WLs, 11 nm SLs). Typical GaAs solar cells with relatively low densities of crystalline defects have diode-ideality factors n equal to or slightly larger than unity,[11,12] where V_{OC}'s are dominated by diffusion current. In Figure 3, we see this $n \sim 1$ situation also applied to our QD cell with thicker SLs and non-QD cell with only WLs. On the other hand, our QD cell with thinner SLs exhibits a steeper rise with n close to 2, as seen in Figure 3. This high-n result demonstrates the advantage of concentrator use for the QD solar cells; for lower solar concentrations, n is approximately 2, but above several suns, n approaches 1, which is the case for state-of-the-art high quality solar cells. The steep rise of V_{OC} in the illumination intensity can be conventionally explained by the dominating recombination current ($n = 2$) possibly due to carrier recombination at the QDs' interfacial defects or other parts, which is suppressed by thickening SLs. Other potential causes of the higher n for the QD cell with thin SLs are miniband formation through the closely packed QD arrays[13] and concentrator-enhanced two-photon-induced carrier escape from the shallow potential well for the 1.0 μm QDs, relative to the case of the 1.1 μm QDs.

Figure 4 summarizes the 1-sun V_{OC} experimental data on the QD ground-state transition energies E for the QD solar cells previously reported[7–10,14–22] as well as that in our present work. The QD transition energies were derived from the peak wavelengths in the photocurrent spectral response, photoluminescence, and electroluminescence data in the references. It should be noted that no significant V_{OC} difference is seen between the cells grown by MOCVD and molecular beam epitaxy (MBE). This is preferable for the commercialization of QD solar cells because of the high production throughput possible from MOCVD growth. The V_{OC} of 1.04 V from Blokhin *et al.*[8] and Bailey *et al.*[21] for their bulk GaAs cells without QD is equal to the V_{OC} for the highest-efficiency bulk GaAs solar cells[23–25] (not the thin-film type cells, which can exhibit $V_{OC} \sim 1.1$ V, Refs. 24 and 26) and is consistent with the collective V_{OC}-bandgap offset data King *et al.* presented,[27] indicating a voltage offset ~0.4 V (i.e., $V_{OC} \sim E$ - 0.4 (V)) for the state-of-the-art solar cells. By contrast, the plot shown in Figure 4 for the QD cells' highest V_{OC} shows a better offset, ~0.3 V. This is a strikingly significant result, indicating that QD incorporation into solar cells can potentially increase efficiency. Many works have presented photocurrent spectral response down to the QDs' ground-state transition energy, while sustaining the cells' output voltages a little higher than those for corresponding bulk semiconductors. In other words, QDs absorb incoming sunlight photons according to their transition energies but the cells' V_{OC} will be higher than those simply following the bandgap offset between the matrix semiconductor (i.e., GaAs in our cases) and the QDs. This strongly indicates a potential to "gain" efficiency by incorporation of QDs.

In summary, we have fabricated a high efficiency InAs/GaAs QD solar cell by a reduced-V_{OC}-degradation MOCVD growth technique with an anti-reflection coating. Efficiencies of 18.7% for 1 sun and 19.4% for 2 suns have been achieved.

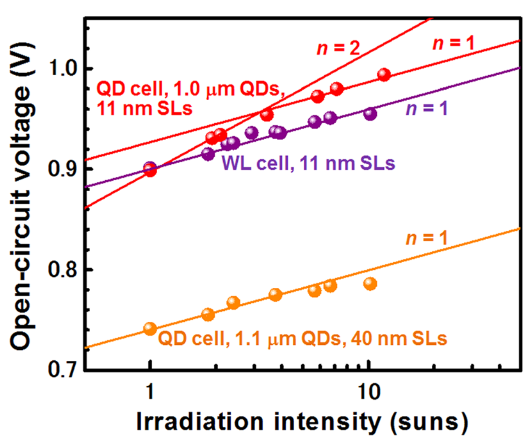

FIG. 3. Dependence of V_{OC} on illumination intensity. The lines are theoretical fitting with $n = 1$ or 2.

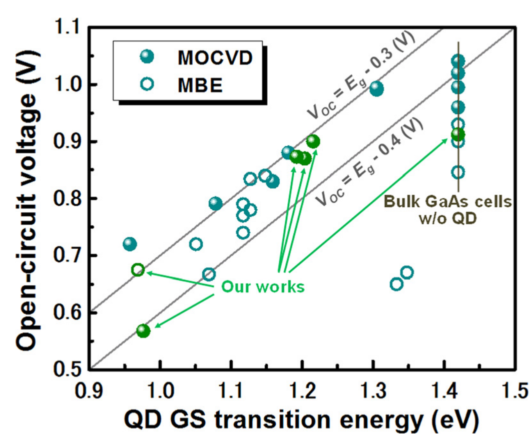

FIG. 4. Summarized experimental V_{OC} data under 1-sun illumination in relation to the QD ground-state transition energies for the QD solar cells previously reported as well as that in our present work. Note that the horizontal axis value $E = 1.42$ eV corresponds to bulk GaAs solar cells without QD. Lines of $V_{OC} = E - 0.3$ and 0.4 (V) are drawn as guides.

Concentrator measurements revealed the advantage of QD use under concentrated illumination because of the steep rise of V_{OC}. We have also found a V_{OC} offset of $\sim$0.3 V from the QD ground-state transition energies, relative to $\sim$0.4 V for state-of-the-art bulk semiconductor solar cells.

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