Development of a Quantum Dot, 0.6 eV InGaAs Thermophotovoltaic (TPV) Converter*

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Abstract

Thermophotovoltaic (TPV) power conversion has to date demonstrated conversion efficiencies exceeding 20% when coupled to a heat source. Current III-V semiconductor TPV technology makes use of planar devices with bandgaps tailored to the heat source. The efficiency can be improved further by increasing the collection efficiency through the incorporation of InAs quantum dots. The use of these dots can provide sub-gap absorption and thus improve the cell short circuit current without the normal increase in dark current associated with lowering the bandgap.

We have developed self-assembled InAs quantum dots using the Stranski-Krastanov growth mode on 0.74 eV $In_{0.53}GaAs$ lattice-matched to InP and also on lattice-mismatched 0.6 eV $In_{0.69}GaAs$ grown on InP through the use of a compositionally graded $InPAs_x$ buffer structure, by metalorganic vapor phase epitaxy (MOVPE). Atomic force microscopy (AFM) measurements showed that the most reproducible dot pattern was obtained with 5 monolayers of InAs grown at 450ºC. The lattice mismatch between InAs and $In_{0.69}GaAs$ is only 2.1%, compared to 3.2% between InAs and $In_{0.53}GaAs$. The smaller mismatch results in lower strain, making dot formation somewhat more complicated, resulting in quantum dashes, rather than well defined quantum dots in the lattice-mismatched case. We have fabricated 0.6 eV InGaAs planer TPV cells with and without the quantum dashes

Introduction

NASA's deep space missions cannot effectively utilize the solar spectrum for power generation using traditional photovoltaic arrays. Instead, the General Purpose Heat Source (GPHS) uses a radioisotope to generate heat which is converted to electricity using thermoelectric power conversion. This power generation method, while reliable, is only about 6.5-9.0% efficient. The use of thermophotovoltaic (TPV) power conversion is an attractive high-efficiency alternative.

Current TPV technology uses planar III-V semiconductor devices with bandgaps that are tailored to the temperature of the source. The infra-red energy emitted by the source is absorbed creating electron-hole pairs within the space-charge region of the p-n junction. The built-in electric field separates the carriers allowing them to perform work in an external circuit. For an 1800° F blackbody source, a 0.6eV bandgap material such as $In_{0.69}GaAs$ is used as the absorber.

The highest efficiency TPV device reported[1] to date is an InGaAs monolithic interconnected module (MIM) using reflective spectral control, measured in a thermophotovoltaic radiator/module system (radiator, optical cavity, and TPV module). Results showed[1] that at a radiator and module temperature of 1039ºC and 25ºC respectively, 23.6% thermophotovoltaic radiator/module system radiant

heat conversion efficiency and 0.79 W/cm^2 maximum TPV radiator/module system power density were obtained. The addition of quantum dots is expected to further increase the efficiency of TPV devices.

The name quantum dot is derived from the fact that as the size of a particle of bulk semiconductor decreases to the nanometer length scale, the electronic properties of the semiconductor change. Once the diameter becomes smaller than the bulk exciton radius, the energy levels in the particle become quantized and the transitions are locked into specific energy states, as opposed to the ordinary band structure present in bulk semiconductors. Each quantum dot behaves essentially as a potential well for electrons trapped within it (*i.e.*, the quantum mechanical "particle in a box"). The energy levels are thus quantized and their energies are inversely related to the size of the box. Therefore, the size of the particle will dictate the threshold energy that it may absorb.

An intermediate band solar cell (IBSC) is a new photovoltaic device which relies upon the presence of quantum dots embedded into an ordinary *p-i-n* type solar cell to provide a theoretical conversion efficiency which is much greater than a conventional solar cell.[2] Theoretical studies predict a potential efficiency of 63.2% for a quantum dot in a p-i-n structure solar cell, which is approximately a factor of 2 better than any state-of-the-art device available today. Similar efficiency enhancements are expected in the case of thermophotovoltaic cells through the insertion of quantum dots in the p-i-n structure.

The presence of an ordered array of semiconducting quantum dots within the junction of the cell results in the existence of an energy band or bands within what in an ordinary semiconductor constitutes its bandgap (see Figure 1). These so-called "mini-bands" will allow for the collection of lower energy (longer wavelength) photons that would normally be inaccessible to the cell. The key to this device is that the low energy photons can be collected without the normal voltage and efficiency degradation associated with using an ordinary narrow bandgap device for converting such photons. Therefore, it is theoretically possible to develop a quantum dot junction that could be incorporated with current TPV cell technology to provide additional conversion in the longer wavelength region of the blackbody spectrum and dramatically improve the overall cell efficiency.

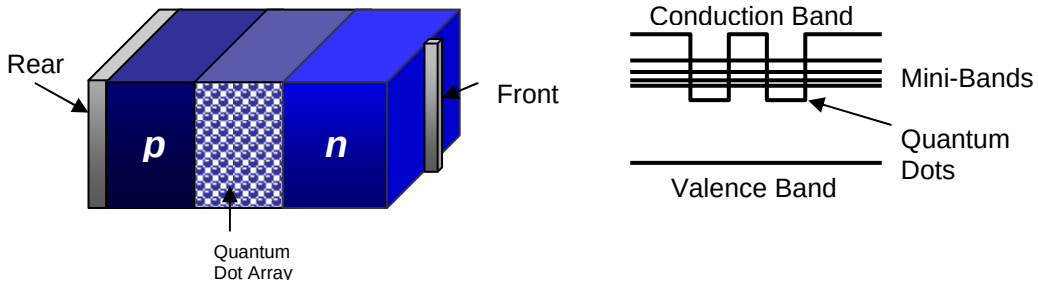

Figure 1.—a) A schematic of an intermediate band thermophotovoltaic cell and b) the energy band diagram for the quantum dot-containing intrinsic region of the device.

Quantum dots (QD) can be formed by the Stranski-Krastanov growth method under modified Metalorganic Vapor Phase Epitaxy (MOVPE) conditions. The dot formation is controlled primarily by the strain between the dot and matrix material. During QD epitaxy the dot material initially wets the surface while the strain energy builds. After a wetting layer of at least one monolayer is deposited, the excess strain energy leads to discrete island formation rather than uniform layer growth. Under appropriate conditions the dot size can be controlled to nanometer size dimensions leading to strong

quantum confinement. The dot size and distribution can be altered by several of the process variables: growth temperature, gas chemistry, growth rate, and subsequent annealing.

Quantum Dot Epitaxy

The materials in this study were grown in a horizontal, reduced pressure, organometallic vapor phase epitaxy (OMVPE) reactor. Trimethyl gallium (TMGa) and trimethyl indium (TMIn) were used as precursor materials, along with phosphine (PH_3), arsine (AsH_3), and 1% AsH_3 in hydrogen. Disilane and dimethyl zinc were used as n- and p-dopants, respectively. The typical growth temperature was 675ºC, while QD deposition temperature was 400-480ºC. All growth runs were performed at a pressure of 600 Torr. The InAs quantum dot morphology was characterized by atomic force microscopy. The variables investigated in this study are the substrate material, growth temperature, and nominal thickness of the quantum dot.

The effect of strain on dot formation is clearly shown in figure 2. The QD material is InAs but the surface layer is GaAs, $In_{0.53}GaAs$, and $In_{0.69}GaAs$ from left to right. This corresponds to strain of 7.1, 3.2, and 2.1% respectively. As the strain decreases, the QD's become more elongated until finally evolving into quantum dashes on the $In_{0.69}GaAs$. The characteristic dot size also increases for reduced strain. The dot diameters range from 25-75 nm on GaAs and increase to 108-140 nm on $In_{0.53}GaAs$ lattice matched to InP. The dashes grown on $In_{0.69}GaAs$ have lengths in excess of 1.0 μm and widths ranging from 180-220 nm.

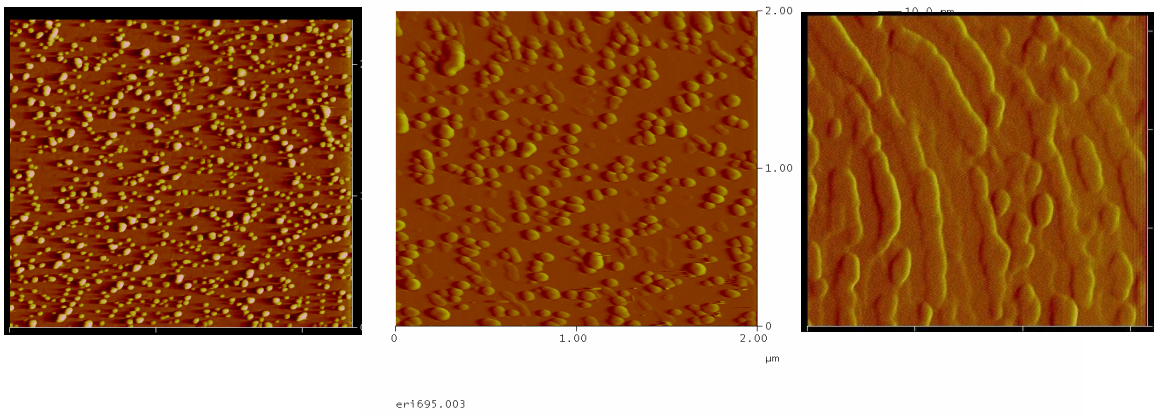

Figure 2.—InAs QDs deposited on different substrates: GaAs, $In_{0.53}$ GaAs, and $In_{0.69}GaAs$.The length scale is 2.5, 2.0, and 1.5 μm for each image left to right.

Figure 3 shows the effect of changing growth temperature for 2.5 monolayer (ML) InAs QD's on $In_{0.69}GaAs$. The temperature was 420, 450, and 480ºC. For lower growth temperatures and thin QD's, discrete dots are visible. As the growth temperature is increased, the dot morphology changes to dashes. This is likely due to increased surface mobility of the indium bearing species at elevated temperature. Another experiment was performed by increasing the QD thickness to 5.0 ML. In this case, all temperatures exhibit dash formation as shown in figure 4. At elevated temperatures the spacing between the dashes increases which also suggests increased surface mobility relative to 420ºC.

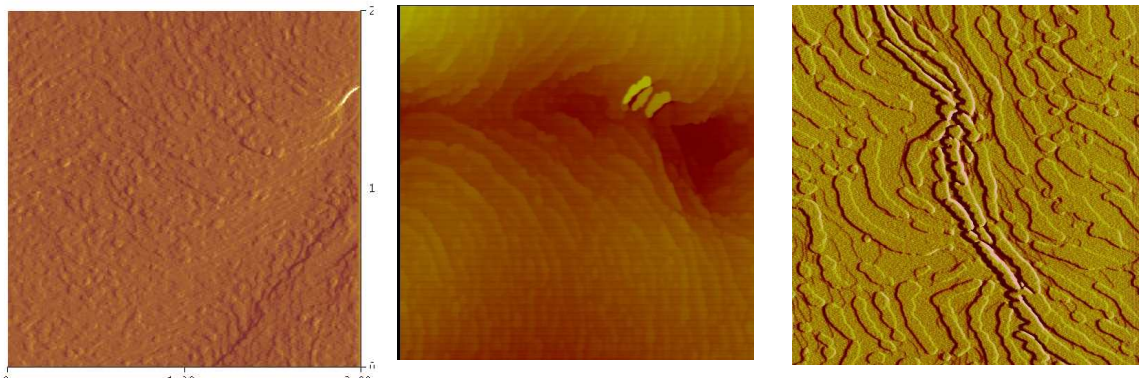

Figure 3.—InAs QDs deposited on $In_{0.69}GaAs$ at 420, 450, and 480C. The length scale is 2.0, 5.0, and 5.0 μm for each image left to right.

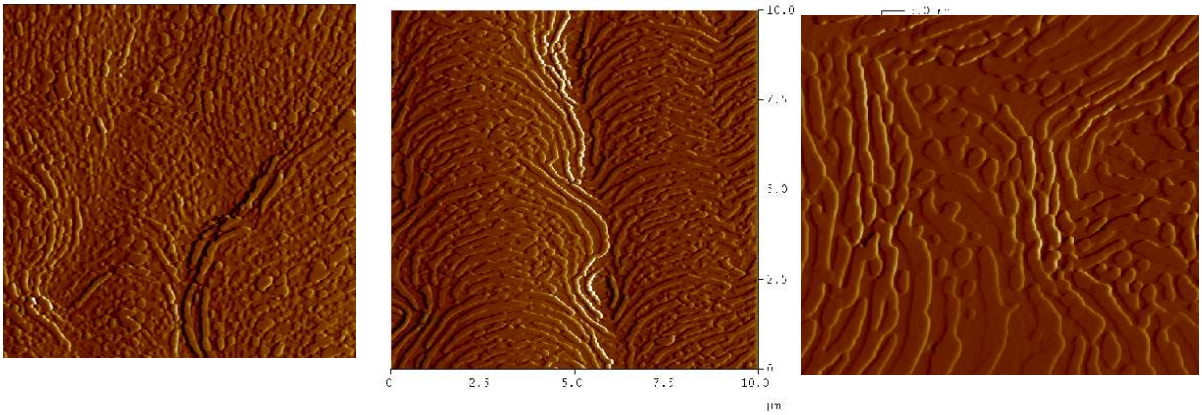

Figure 4.—InAs QDs (5.0ML) deposited on $In_{0.69}GaAs$ at 420, 450, and 480C. The length scale is 5.0, 10.0, and 5.0 μm for each image left to right.

Results and Discussion

0.6 eV TPV cells were grown by OMVPE on InP substrates using a modified structure used in many laboratories.[1,3,4,5] It consists of a 0.6 eV InGaAs cell grown on lattice mismatched InGaAs using our proprietary[6] buffer structure. The QD active region was inserted at the p-n junction within the InGaAs cell. The QD period consists of an InAs QD layer followed by a 15 nm InGaAs cladding.

0.6 eV TPV cells were processed using standard photolithographic techniques. AM0 conversion efficiencies were measured at 25 °C using a single source, Spectrolab X25 solar simulator. Spectral response measurements were performed to determine the external quantum efficiency (EQE) of the cells. Four designs were tested: Baseline TPV with no QD's, TPV with 5 periods of 5ML QD, 10

periods of 5 ML QD, and 10 periods of 10ML QD. The results are tabulated in Table 1. None of the devices had anti-reflection coating.

QD Structure	Area (cm2)	Isc (mA)	Voc (mV)	FF (%)	Efficiency (%)
None	1.0	44.7	216.7	49.5	3.5
5 period 5ML InAs	1.0	32.7	177.7	42.9	1.82
10 period 5ML InAs	1.0	25.3	180.8	25.4	0.85
10 period 10ML InAs	1.0	44.0	163.8	42.1	2.22

Table 1.—Summary of results for 0.6eV TPV's with and without QD's.

In all cases the introduction of QD's leads to a degradation of cell efficiency. This is generally manifest as a penalty in V_{oc} and I_{sc}. Interestingly, the 10 period, 10ML device has an I_{sc} approaching the baseline performance. This implies that the QD's must have sufficient size inside a device structure.

Figure 5 shows typical I-V curves for the baseline and 10-period, 10ML device. Isc is comparable in both cases, with the QD device exhibiting a lower Voc. In order to verify that the cladding material is not contributing to the degradation a separate device was fabricated that contained only the InGaAs cladding material at the p-n junction but no QD's. This device operated nearly identically to the baseline structure indicating that the penalty in performance in these devices is due to the QD's and not the cladding material.

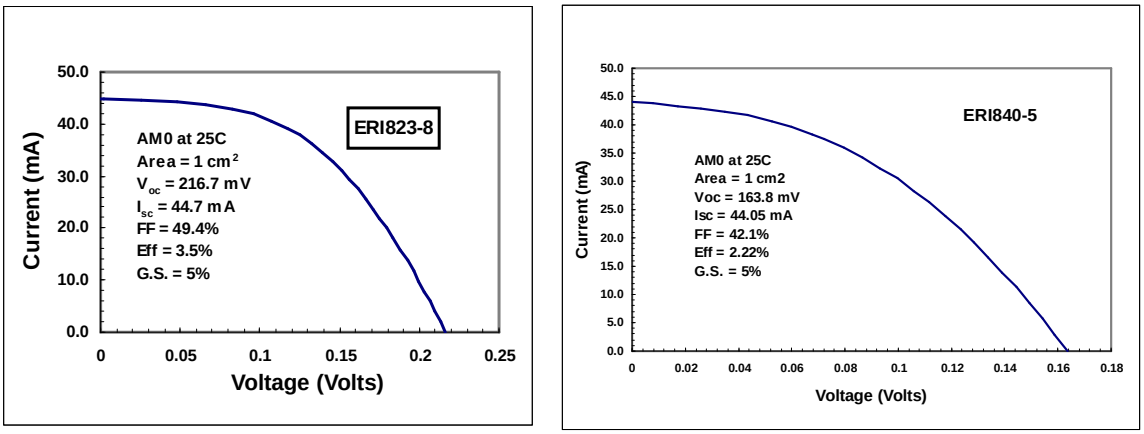

Figure 5.—I-V curves for 0.6eV TPV cells without QD (left) and with 10 period, 10ML QD.

Figure 6 shows the EQE spectra for the baseline TPV and the 10 period, 10ML QD sample. If QD's were indeed absorbing sub-bandgap photons, the EQE should exhibit absorption peaks corresponding to quantum confined states at longer wavelengths. Figure 6 indicates a shift to longer wavelengths for the QD device. However, this amount of shift is more readily explained by a slight compositional shift of the bulk InGaAs material.

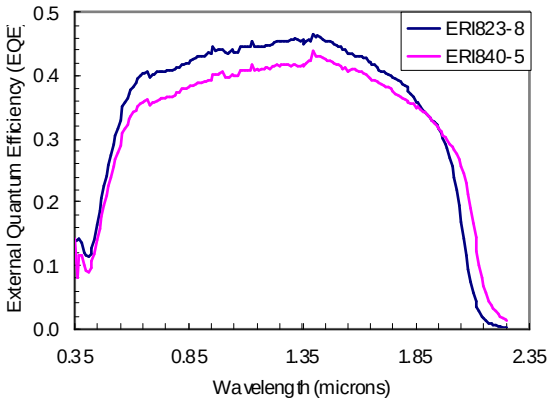

Figure 6—EQE data for 0.6eV TPV with (pink) and without (dark) QDs. The spectral shift for the QD sample is due to a slight compositional shift in the bulk InGaAs.

Summary

Several aspects of quantum dot growth on lattice-mismatched InGaAs have been investigated. As the strain between the QD and surface composition decreases, distinct QD's become dash-like in nature. This tendency increases for elevated temperatures. The effect of the growth temperature is a primary factor in dot formation and distribution, which is explained by the influence of temperature on surface diffusion. At present, incorporating multiple QD layers into the active region of a 0.6 eV TPV cell causes a decreased efficiency due to a reduction of Isc and Voc values. By using a QD structure containing 10 periods, 10ML QD's the Isc penalty is eliminated, though the Voc penalty persists. Continued optimization of the QD epitaxy is expected to resolve these problems, resulting in the realization of enable sub-gap absorption, and higher cell efficiency.

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