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InAs and InP Quantum Dot Molecules and their Potentials for Photovoltaic Applications

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ABSTRACT

Self-assembled InAs and InP quantum dot molecules (QDMs) are grown on GaAs substrates using different molecular beam epitaxial (MBE) growth techniques. The structural and optical properties of the two types of QDMs are then compared and reported. Multi-stack high-density (10^{12} cm^{-2}) InAs QDMs are grown and when inserted into GaAlAs/GaAs heterostructure results in high-efficiency solar cells. As an alternative to InAs, InP QDMs are grown by droplet epitaxy of In and annealing under P_2 pressure. While the number of quantum dots per QDM in the case of InP is in the range of 10 to 12 dots, those in the case of InAs can be smaller or much larger depending on exact growth parameters prior to QD growth. Photoluminescence (PL) measurements show that while InAs QDMs provide room-temperature optical output that peaks at 1.1 eV, InP QDMs have no PL output, possibly due to crystal defects created by low-temperature processing associated with droplet epitaxy. Discussion on the practicality of our QDMs as material for intermediate band solar cells is also provided.

Keywords: quantum dot molecules, molecular beam epitaxy, photovoltaic, droplet epitaxy

INTRODUCTION

III-V compound semiconductors are useful for high-efficiency solar cells, especially at high concentrated sunlight because the bandgaps, temperature coefficients and various structural and optical properties can be controlled by varying the alloy compositions in binary, ternary and quaternary compounds.(1-3) As an example, conversion efficiency on the order of 35-40% under concentrated sunlights (200-600 suns) can be realized by III-V multi-junction tandem cells.(4-6) III-V semiconductor based concentrator systems is now commercially available, with a potential for cost reduction of photovoltaic (PV) systems in the long run.(7) The success of such systems stems from the fact that they use small area, high efficiency cells. One 4-inch wafer yields a few hundred pieces of high efficiency tandem cells for a concentrator system. Cheaper substrates such as Ge can also be used to grow GaAs-based tandem solar cells for space and concentrator system applications.(8)

Among III-V compound semiconductors, GaAs-based solar cells such as GaAlAs/GaAs, InGaP/GaAs and InP/GaAs are mostly utilized.(9-10) InP/GaAs in particular is the most promising semiconductor materials for high-efficiency solar cells because of suitable bandgaps and associated optical/electrical properties.(11)

Bandgap engineering is important and a basis for multi-junction cells that can absorb a wide solar spectrum for higher PV output. Multi-junction tandem solar cells based on III-V compound semiconductors are a topic that receives a great deal of attention.[12-14] However, these structures are complicated in terms of design and fabrication because of stringent growth requirements (lattice matching) and the needs to achieve good electrical contacts to both the upper wide bandgap cells and the lower narrow bandgap cells.

Our approach for high-efficiency solar cells is to make use of quantum dot (QD) nanostructures in single-junction III-V compound semiconductor. Comparing to the tandem cells, our approach is simpler in terms of cell design and fabrication. In our approach, self-assembled QDs are grown via Stranski-Kratanow (SK) mode which is based on lattice-mismatch, strained semiconductors. SK dots are defects-free and, therefore, are useful for various device applications, such as lasers and nano-photonic devices.[15-16] The density of as-grown SK dots in the range of 10^9-10^{10} dots/cm^2 is, however, too small for effective photon conversion: A much higher value of 10^{12} cm^{-2} is needed.[17] With our thin-capping-and-regrowth MBE process,[18] InAs QD ensembles called quantum dot molecules (QDMs) are grown with dot density of 10^{10}-10^{11} cm^{-2}. Stacking of QDMs allows the critical dot density of 10^{12} cm^{-2} to be reached. Multi-stack high-density InAs QDMs are subsequently inserted into GaAlAs/GaAs heterostructure solar cells in order to achieve high efficiency. We have demonstrated multi-stack high-density InAs/GaAs QDM heterostructure solar cells with a conversion efficiency of 25.9% under 100 mW/cm^2 AM1 illumination.[19] Improved PV performance at high concentration sunlight has also been demonstrated and believed to result from the zero dimensionality of this quantum dot nanostructures.[20]

In addition to InAs on GaAs, we also explore an alternative QD material, InP/GaAs, which is believed to be able to provide better photovoltaic efficiency. InAs/GaAs interface has a lattice mismatch of 7%, while InP/GaAs interface has a smaller mismatch of 3.8% . $In_{0.49}Ga_{0.51}P$ (lattice-matched to GaAs) is used as a buffer and a capping layer for InP QDs. In the preparation of InP QDMs, we use droplet epitaxy followed by annealing under P_2 pressure to create InP QDMs with 10-12 QDs per QDM.

In order to utilize InP QDs for photovoltaic cells, high dot density is needed. One of the technical barriers is the growth of 10^{12} InP QDs/cm^2. The present droplet epitaxy technique we developed yields a low dot density of less than 10^8 dots/cm^2. Therefore, conventional MBE technique at higher growth temperatures using higher lattice-mismatched materials is under investigation. Nevertheless, by repeating the growth process for several cycles similar to the thin-capped-and-regrowth technique of InAs QDMs, high InP dot density may be achieved.

GROWTH OF InAs AND InP QDMS

(100)-GaAs substrates are used as the starting material for the growths of InAs and InP QDMs in a solid-source MBE machine (32P RIBER). After oxide desorption, 300 nm of GaAs buffer layer is grown at 500°C.

For the growth of InAs QDMs, InAs QDs are grown on the GaAs buffer layer at 500°C. Then, the substrate temperature is reduced to 470°C in order to thin cap the as-grown InAs QDs by GaAs. Thin capping at low temperature is conducted so that anisotropic strain fields cause the change of QD shape, from circular to elongated nanostructures with a nanohole in the middle of each as-grown QD. Without any interruption after the formation of the nanohole template, regrowth of QDs is continued at the same substrate temperature of 470°C. At 1.2-ML regrowth thickness, self-assembled InAs QDMs are formed as shown in the atomic force microscopy (AFM) image in figure 1.[18] By repeating the thin-capping-and-regrowth MBE process for several cycles, high density InAs QDMs are achieved. Multi-stacks of high-density InAs QDMs having dot density of 10^{12} cm^{-2} are then overgrown with additional layers to from GaAlAs/GaAs heterostructure and the electrical characteristics will be reported in the next section.

For the growth of InP QDMs, a different MBE growth technique is used. In order to from InP QDs, appropriate lattice mismatch is needed. InP/GaAs interface has a lattice mismatch of only 3.8% and low dot density can be expected. In order to create energy barrier, $In_{0.49}Ga_{0.51}P$ which is lattice-matched to the GaAs substrate is used as a buffer and also a capping layer to the underlying InP QDs. The reason that we choose InGaP layer is because it has a wider bandgap comparing to GaAs (1.43 eV) whose bandgap is too close to InP (1.38 eV). Droplet epitaxy of In is conducted as follows: 3.2 ML of In is grown at of 250°C at a growth rate of 1.6 ML/sec. The In droplets are then annealed at 200°C under P_2 pressure of 4×10^{-6} torr. The P_2 beam is produced from a GaP effusion cell. After 10 minutes of annealing, InP quantum rings (Q-rings) are obtained as shown in figure 2. The number of QDs per QD-ring is 10-12 dots. However, the overall dot density of InP QDMs is still too low (less than 10^8 dots/cm^2) for PV applications. In order to increase the dot density, different compound composition with higher lattice mismatch would be needed. Therefore, appropriate capping materials for InP QDMs are under investigation using conventional MBE growth process with higher growth temperatures.

EVALUATION OF InAs AND InP QDMS

Strong photoluminescence (PL) at room temperature from high-density InAs QDMs is detected, indicating good dot quality. One stack of high-density InAs QDMs provides a PL peak at 1.075 eV with a full-width-at-half-maximum (FWHM) value of 76 meV as shown in figure 3. Five-stack InAs QDM sample gives stronger photoluminescence with PL peak at 1.053 eV and the same FWHM value of 76 meV. Red shift of PL peak implies that the 5-stack QDM sample has, on the average, larger dots. The FWHM values indicate that both QDM samples have equally uniform dots.

No room-temperature PL signal from InP QDM sample is observed. We believe that the absence of the PL signal is caused by crystal defects associated with low temperature processes and low dot density associated with the formation of QDs on small lattice-mismatched systems.

Form a theoretical point of view, the integration of QDs in a solar cell structure gives rise to an intermediate band as show in the schematic diagram in figure 4. The theory of intermediate band solar cells has been perposed by Luque and Marti. [21] The photocurrent is increased by the absorption of sub-bandgap photon without degrading voltage. Two-step photon absorption among sub-bandgap could give extra generation of electron-hole pairs through pumping from valence band to intermediate band and from intermediate band to conduction band. For effective two-photon absorption process, the position of the intermediate band should be at the middle of the bandgap. Meeting this requirement will result in a high efficiency solar cell.

InAs has a small bandgap of 0.34 eV. When InAs QDs are inserted in a GaAs matrix, the quantized energy states would lead to spectral response at long wavelengths beyond the absorption edge of GaAs bandgap (1.43 eV). On the otherhand, InP having 1.34 eV bandgap would provide higher quantized energy states defined by its nanostructure parameters such as QD size, barrier height, etc. Therefore, we can expect a good response at shorter wavelengths which make up a major portion of the solar spectrum. However, a wide bandgap material ($E_g > 3$

eV) is necessary to cap the InP QDMs so that their quantized energy states would function as an intermediate band in the overall solar cell structure.

The quantized energy state of InAs QDMs in the GaAs matrix is approximately 1.1 eV, as indicated from the PL result in figure 3. This value is too close to 1.43 eV, the bandgap of GaAs. A wider bandgap close to 2 eV is required to realize high-efficiency cells. This can be achieved using GaAlAs buffer and capping layers.

In the case of InP with a bulk 1.34-eV bandgap, the quantized energy state of InP QDMs is, therefore, located at a higher energy level. This provides an intermediate band for short wavelength absorption, matching the visible region of the solar spectrum. Based on published PL results,[22, 23] InP QDs have a PL peak at 1.6 eV at room temperature. Therefore, a wide bandgap (~3 eV) capping material is needed.

To confirm the practicalities of these proposed ideas, multi-stack high-density InAs QDM solar cells are fabricated and their electrical performance measured under different sunlight conditions. The schematic structure of QDM solar cell is shown in figure 5. Multi-stack high density QDMs are inserted in the n on p heterostructure of GaAlAs/GaAs. Typical InAs QDM solar cell provides conversion efficiency as high as 25.9% under AM1 100 mW/cm^2 solar illumination. The spectral response beyond the GaAs band edge of 850 nm, extending to long wavelength regions, has been observed in InAs QDM solar cells.[19] At high sun number, InAs QDM solar cells have stable performance with super-linear increase of their short-circuit current density as shown in figure 5.

CONCLUSIONS

InAs and InP QDMs are grown by modified MBE techniques. Their structural, electrical and optical properties are then evaluated. InAs QDMs, when inserted into GaAlAs/GaAs heterostructure, show good response at long wavelengths beyond 850 nm, the absorption edge of GaAs. Current-voltage characteristics indicate that InAs QDM solar cells have high efficiency and good, stable performance at concentrated sunlight conditions. InP QDMs with their prominent QD-rings feature, on the other hand, do not show photoluminescence at room temperature. This is possibly due to crystal defects created by low-temperature processing of droplet epitaxy. Improvements of InP QDM quality and density are required if this new nanostructure material is to be used as efficient PV cells. In addition, suitable capping materials with wide bandgaps are needed for both InAs and InP QDM-based intermediate band solar cells.

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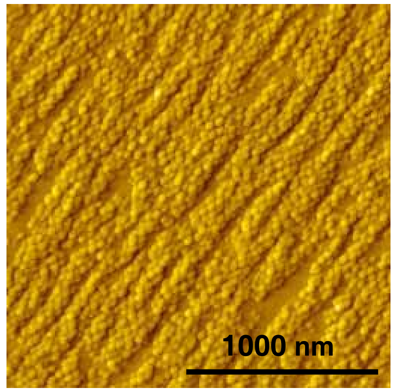

Fig. 1 An AFM image of high-density InAs QDMs grown by multi-cycle thin-capping-and-regrowth MBE process.

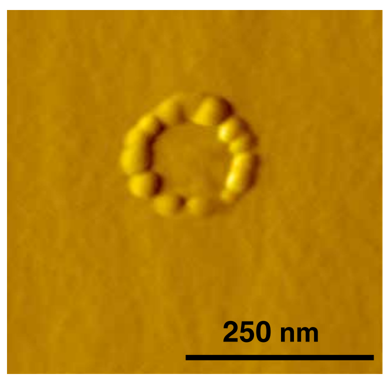

Fig. 2 An AFM image of InP QDMs having QD-ring feature.

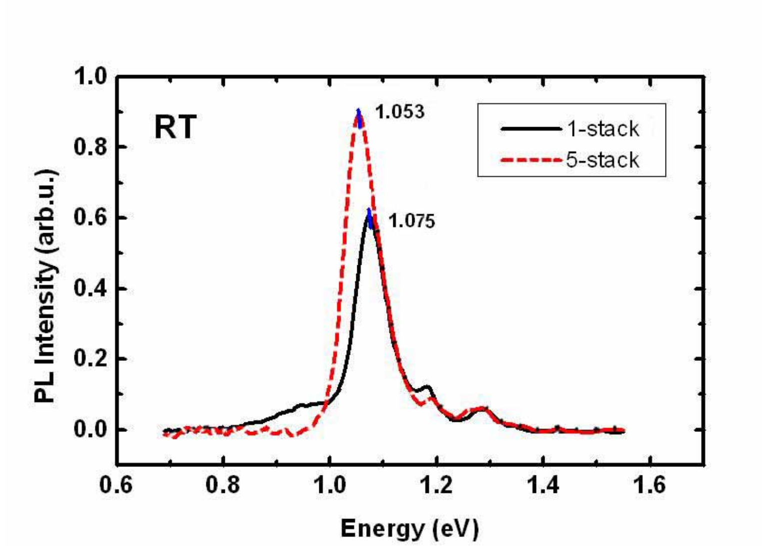

Fig. 3 PL spectra of 1- and 5-stack high-density InAs QDMs

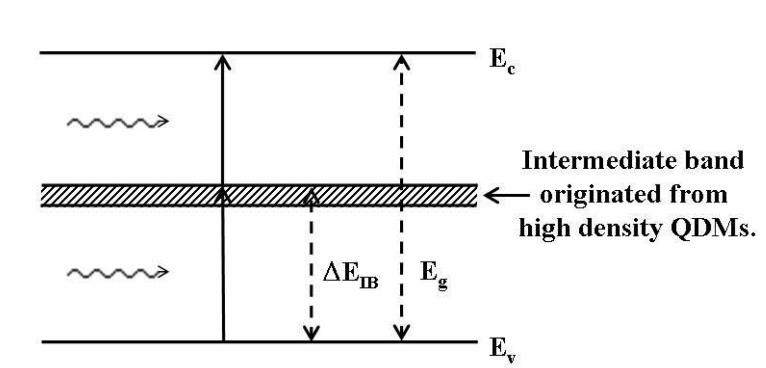

Fig. 4 A schematic energy diagram showing the two-photon absorption process.

ΔE_{IB} : Intermediate band energy of QDMs.

E_g : Bandgap of capping semiconductor material.

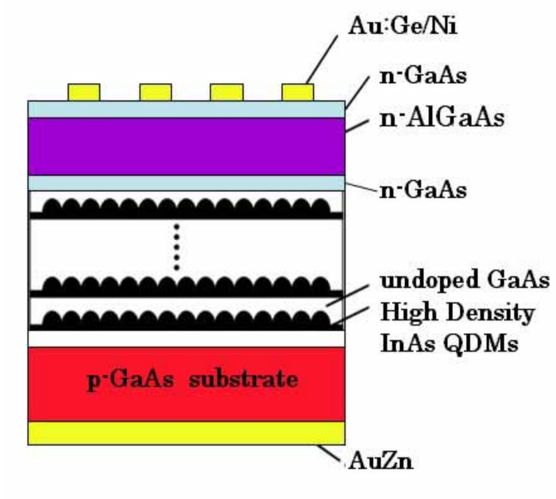

Fig. 4 Schematic structure of QDM solar cell.

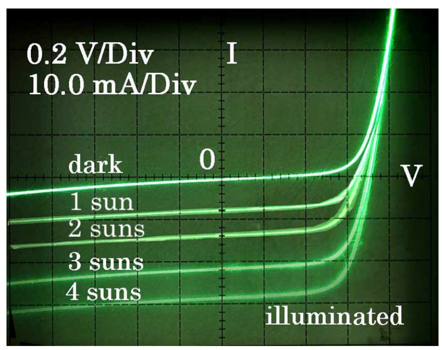

Fig. 5 I-V curves of InAs QDM solar cells at various sun intensities (1~4 suns).