GROWTH OF InAs QUANTUM DOTS ON GaAsSb FOR THE REALIZATION OF A QUANTUM DOT SOLAR CELL

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ABSTRACT

The InAs/GaAsSb quantum dot/barrier material system has been identified as a candidate for implementing the quantum dot (QD) solar cell for an Sb content of ~ 12%. We present results from the growth of this system on GaAs substrates by Molecular Beam Epitaxy (MBE). The results show that the growth of GaAsSb requires special care in order to ensure the highest quality interface and also to maintain the Sb composition. When InAs QDs are grown on the GaAsSb, the role of strain in determining the properties of the QDs is seen to be profound. Results from PL studies show that the sizes of the QDs are controlled by the GaAsSb layer thickness and hence the residual strain at the GaAsSb surface. In addition a change from type I to type II transitions can be affected by this method. The implications of these results plus the influence of the substrate choice, and so the strain, on the system properties will be discussed in terms of a QD solar cell design with a strain balanced design enabling a much larger active region and hence higher absorption.

INTRODUCTION

Novel concept solar cells are proposed structures that have the potential for vastly exceeding the conventional limits of energy conversion efficiency. All of the proposed structures rely on the exploitation of either processes not considered in semi-classical approaches or exploiting processes conventionally considered detrimental. The intermediate band solar cell [1] is a novel concept solar cell exploiting processes not considered in conventional solar cell designs. The inclusion of a third carrier band within the band gap of a host or barrier structure sees the number of absorption and emission processes increase from 2 to 6 with a population of carriers being maintained in the intermediate band. This sees light generated current increase due to increased absorption of lower energy photons. This increase comes without sacrificing the high voltages due to the barrier and so efficiencies comparable to those for three solar cell tandem structures are predicted.

In recent years, the search for a method for the realization of intermediate band solar cells has received increasing attention both from the theoretical and experimental points of view [2,3]. A considerable amount of the debate has centered on the choice of materials system that will allow the maintaining of three separate carrier populations each with its own associated Fermi level [4]. When the transitions between these separate carrier populations can be guaranteed to be radiative then a significant efficiency boost is found in comparison to a standard single band gap solar cell [5]. The key physical process required to provide the efficiency boost, namely, simultaneous multiple radiative transitions (SMRT) may be observed in quantum dot (QD) or quantum well (QW) structures.

The central idea behind the QD solar cell is illustrated in Figure 1. A highly dense array of QDs are physically positioned in close enough proximity so that the wavefunctions associated with the bound states overlap. The overlap should be significant enough that the QDs act as a band. The QD solar cell needs not just a highly dense closely spaced array of QDs but the QDs should be relatively homogeneous in size [6].

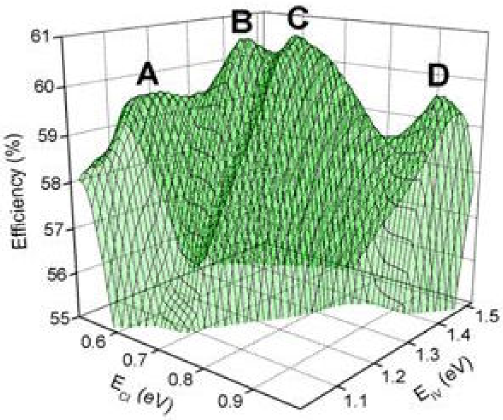

Figure 1. Limiting efficiency contour for an intermediate band solar cell under 100x concentration AM1.5 spectrum.

There are further requirements for obtaining the necessary simultaneous radiative transitions for use in a solar cell. The band offset between the QDs and the barrier should be zero (to within 3/2 k_BT) for either the conduction band or valence band. The band chosen depends on the carrier type for quantum confinement and is essentially arbitrary. The requirement of a zero band offset has been shown to be necessary to avoid open circuit voltage losses associated with having confinement of both carrier types [7]. As well as this it will help in simplifying the analysis of any results to more accurately determine the existence of the simultaneous radiative transitions.

One materials system identified as having the potential to fulfill all of these requirements, namely the InAs/GaAsSb system is the subject of this paper. Starting by looking at the motivation for studying this system some of the practical issues in the epitaxial growth will be examined as well as some of the advantages inherent in this system.

The role of strain in this system is also addressed by looking at results from time resolved photoluminescence and modeling of the band structure. It is concluded that the strain is of extreme importance in this system and influences the whole structure, even the choice of substrate.

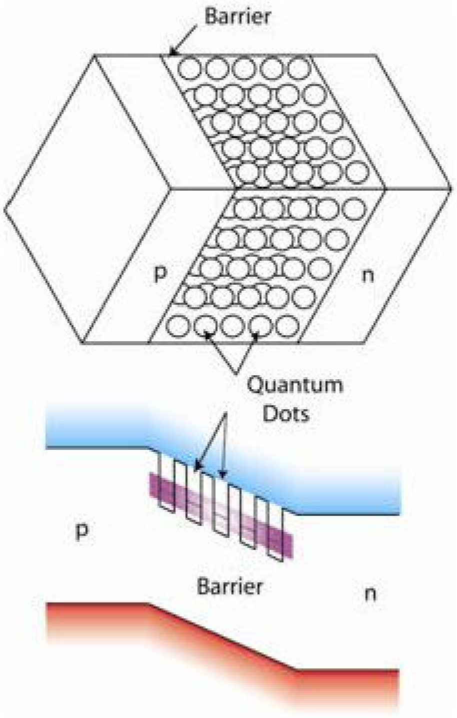

Figure 2. Schematic of a quantum dot solar cell showing the key design principle of the overlap of bound state wavefunctions

THE InAs/GaAsSb MATERIALS SYSTEM

Using these required properties as search criteria several materials systems have been identified. The most promising in terms of the search criteria are summarized in Table I. It must be noted that the selection of these materials was done with no detailed strain considerations. Of the materials systems found, the InAs (QD) / $GaAs_{0.88}Sb_{0.12}$ (barrier) system has been chosen for further investigation for a number of reasons. Firstly, the QD species is binary, effectively removing the need for ternary composition control in a system with highly position dependent strain. Secondly, Sb can be used to boost the QD areal density as well as passivate the surfaces of the QDs giving better optical performance [8].

An added bonus is that GaAsSb barriers are compatible with methods for altering the growth surface prior to QD growth giving near maximum areal coverage [9]. Despite these advantages the materials system does have several issues that need to be addressed. A very practical issue is that of controlling the GaAsSb composition in order to ensure a zero valence band offset. The ready exchange of Sb and As makes growth surface modifications possible along with the ensuing higher dot densities. However, this also means that control of the As and Sb proportions in grown layers is more challenging than for a III-III-V compound such as InGaAs. This ready exchange will also have implications for the interdiffusion of Sb and As in grown quantum dots affecting the electronic and optical properties. Finally, the choice of substrate is important, since, as the results presented show, the strain in the grown layers has a profound impact on the properties of the final structure.

Barrier	Quantum Dot	E_{CI} (eV)
GaAs	$InP_{0.85}Sb_{0.15}$	0.49
GaAs	$InAs_{0.4}P_{0.6}$	0.49
$GaAs_{0.88}Sb_{0.12}$	InAs	0.83

Table 1: Summary of candidate material systems for use as a QD solar cell. E_{CI}(eV) is the energy between the barrier conduction band edge and the bound state of the QD.

EXPERIMENTAL ASPECTS

All of the MBE growth was performed in a solid source Applied EPI Gen III MBE system. The base pressure of the growth chamber was around 2×10^{-10} torr for all growth runs. *In-situ* RHEED was used to monitor the growth process as well as controlling the growth rate. The RHEED system consists of a commercial 12 keV electron gun focused onto substrate surface at a grazing angle with the diffracted beam incident on a phosphor-coated screen. A CCD camera monitored the diffraction patterns with commercial software used to analyze the patterns for in-situ determination of the growth rate. The arsenic and antimony fluxes were controlled by separate valved crackers with the cracker zone temperatures set to deliver As_2 and Sb_2 respectively.

All of the samples were grown on EPI ready (001) semi-insulating GaAs wafers with the substrate temperature measured by both a thermocouple and a pyrometer. The GaAs substrate was first heated to remove the native oxide under As_2 rich conditions. De-oxidation was confirmed by observation of the RHEED pattern and the pyrometer and thermocouple calibrated to 585 C. The substrate was then heated to 620 °C for 10 min to completely remove the entire oxide residue. After oxide desorption, the temperature was dropped to 580 C and a 200 nm thick GaAs buffer was grown to planarize the surface. The background As_2 pressure was maintained at 5×10^{-6} Torr throughout all of the growth. The RHEED pattern showed a 2×4 reconstruction and the growth rate could be determined by observing the intensity oscillations in the RHEED peaks in 2 x direction. After determining the growth rates of GaAs, GaAsSb and InGaAs another 200nm of GaAs was grown.

The InAs growth mode transition from 2D layer to 3D island growth was monitored by observing the change in the *in situ* RHEED pattern to a chevron pattern along the [1-10] azimuth. After the InAs QDs were grown, uncapped samples were immediately rapidly cooled down to freeze the QDs on the surface for characterization by *ex-situ* AFM. Capped samples had further GaAsSb grown immediately over the QDs with a 75nm GaAs cap finishing the sample. The Sb composition was determined by double crystal X-ray diffraction measurements.

GROWTH OF GaAsSb ON GaAs

Optimizing the GaAsSb/GaAs interface

The ready exchange of Sb and As at the growth surface means that some care must be taken when growing GaAsSb on GaAs. Experience has shown that the flux of Sb_2 needs around 20s to stabilize to its steady value. This would mean that the Sb composition would slowly increase initially as the layer is grown. For thin layers of GaAsSb we should therefore open the Sb shutter prior to growth long enough to obtain a steady flux of Sb. Previous reports have also indicated that the growth temperature may influence the composition variation in epitaxial layers [10].

Samples were grown of a 5x superlattice of 5nm/25nm GaAsSb/GaAs with a 75nm cap on GaAs SI substrates at 500C. The Sb flux was set to 8.2 x 10^{-8} torr. Before each of the GaAsSb layers were grown the Sb shutter was opened for either 0s, 30s or 60s. The samples were then all analyzed by X-ray diffraction to determine the composition of each and to detect the presence of misfit dislocations.

In Figure 2 we see that there is broadenening of the curve at the bottom for the 0s and 60s samples with respect to the 30s sample. This broadening is indicative of misfit dislocations being generated in the structure. So it can be deduced from these results that the optimum procedure for growth with low dislocation density is a 30s Sb/As soak before any growth of GaAsSb on GaAs.

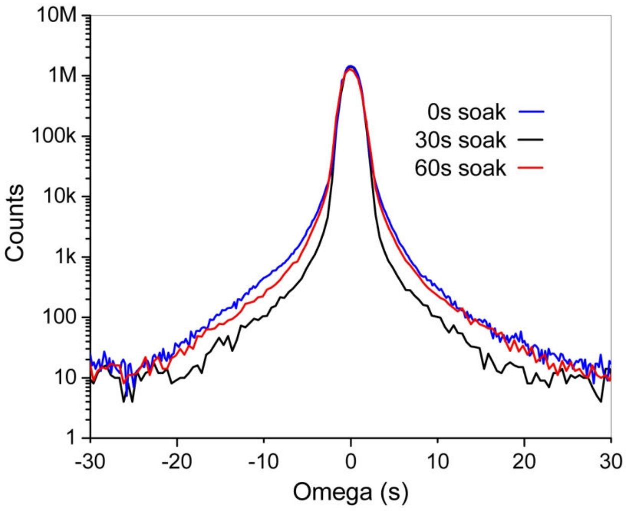

Figure 2: Double crystal axis diffraction patterns for samples with Sb/As soak times of 0s, 30s and 60s respectively.

Control of GaAsSb Composition

GaAsSb is a III-V-V ternary compound, which means maintaining the desired composition is more challenging then for a III-III-V compound such as InGaAs. This is because the Group V elements (As,Sb) are more volatile than their Group III counterparts. The net result is that the composition is determined by not just the ratios of the Group V fluxes but also by the growth temperature as the sticking coefficients of the Group V elements are highly temperature dependent.

To determine the relationship of the Sb composition with the growth temperature and fluxes of Sb and As a series of samples were prepared. Each sample consisted of a 5x superlattice of 5nm/25nm GaAsSb/GaAs layers with a 75nm GaAs cap. The growth temperature was either 470 C ,500 C or 530 C as read by pyrometer. The flux was varied first from approximately 3.1 x 10^{-8} torr to 8.2 x 10^{-8} torr. Extra values of flux were obtained as deemed necessary.

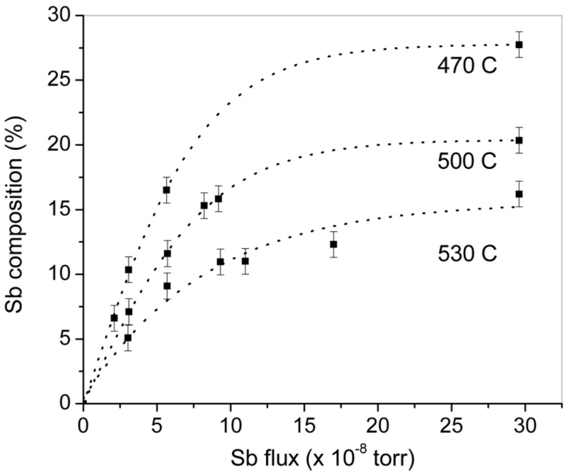

Figure 3: Sb percentage in GaAsSb layers grown by MBE on GaAs substrates. The As pressure was 5.0 x 10^{-6} Torr for all samples.

Figure 3 shows the composition of GaAsSb layers grown on GaAs substrates. The error bars represent the ±1% uncertainty in Sb composition estimated in determination by double crystal axis XRD. The results are for coherent strained layers of GaAsSb, with no relaxation. The compositions found would be expected to be different if layers of GaAsSb have partially or fully relaxed. As can be seen, when growing this material care must be taken with regards to the growth temperature particularly when a specific composition is sought.

The most notable feature of these curves is that the increase in Sb composition is initially sharp with the gradient decreasing as the Sb flux increases. Indeed the 530 C curve can be seen to be almost completely flattening at roughly 12% Sb composition. This agrees with previous reports [refs] for relaxed layers of GaAsSb on GaAs where similar behavior of the composition was reported. This loose pinning of the composition has been attributed to the inability of the alloy to effectively accommodate different atomic sizes and bond lengths [11].

The implications for the growth of GaAsSb are that since we would like to have good control over the Sb composition then the growth should be done at higher temperatures. The reasoning is that if the flux is set to be in the region where the composition change is very low even if the flux varies during growth the effect on the composition may be negligible. In short the procedure is made robust to flux changes, provided we have good control over our temperature. The results found here suggest a growth temperature around 530 C should be used.

GROWTH OF InAs QUANTUM DOTS

One of the key properties of Sb is it's perceived ability to lower the surface energy of a growth surface and hence it's ability to act as a surfactant. The net result of this is that when InAs QDs are grown on GaAsSb the QD density increases substantially compared to that when InAs QDs are grown on GaAs. The resulting increase in QD density as the Sb content is increased is reported elsewhere [ref]. The GaAsSb buffer layer was grown with a thin (5ML) GaAs cap before QD growth in that case but there is another more subtle method that can be used to reduce the surface energy significantly.

The method relies on the ability of Sb and As to readily exchange with each other at the growth surface. First reported by Yamaguchi et al. [12] the procedure is to close the As flux using an automated valve positioner. Immediately following this the Sb shutter is opened so that the growth surface sees a Sb-rich overpressure. With the exchange of Sb for As, the surface is transformed into Ga(As)Sb with the Sb content increasing as the time of exposure increases. Ideally only 1 monolayer of Ga(As)Sb is induced at the surface.

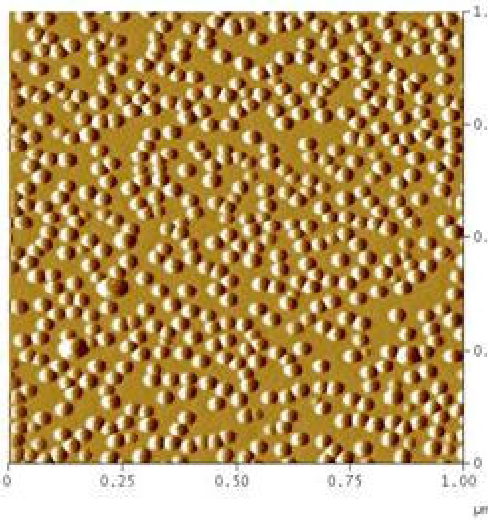

Figure 4: AFM scan of sample with ~ 2 monolayers of InAs quantum dots on a GaAs substrate with ~ 1 monolayer of GaSb at the interface.

The change in the surface is easily monitored by observing the RHEED signal to see the transition from 2 x 4 reconstruction to 1 x 3 reconstruction. When this transition occurs it is tempting to think the first monolayer is GaSb. In truth the transition to a 1 x 3 reconstruction will occur when there is still As in the surface layer as shown by numerous studies [13]. It is, however, a convenient marker since the Sb content will be quite high and so the strain in the surface monolayer will be very high.

The result of such a procedure is displayed in the AFM scan of Figure 4. The number density of quantum dots was found to be ~5 x 10^{10} cm^{-2} a value considerably above the usual reported number densities for InAs on GaAs. This increase in number density has not been maximized with no optimization of the procedure in terms of temperature, deposition amount or growth interrupts having been done.

Effects of Strain on QD Properties

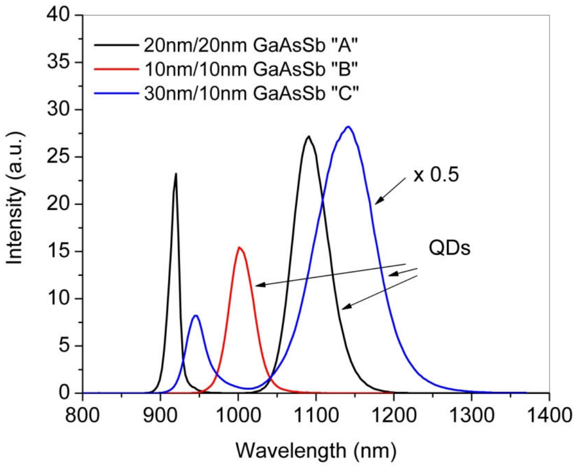

Figure 5: Photoluminescence spectra at 4K for three InAs QD samples (~2ML) with various $GaAs_{0.88}Sb_{0.12}$ buffer/cap combinations.

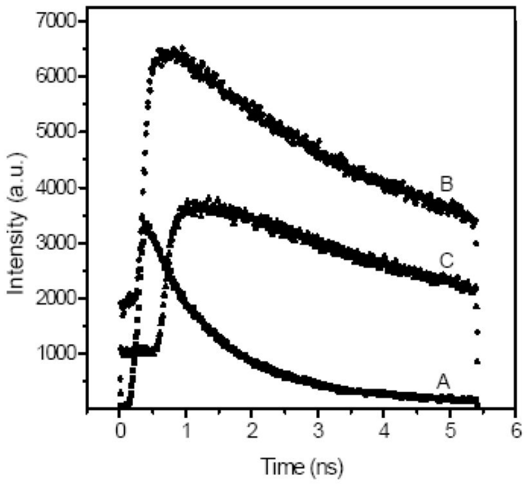

Figure 4: (a) Time resolved PL (TRPL) spectra for samples A, B and C at 4K.

As stated earlier the choice of substrate to grow the InAs/GaAsSb system on is critical to the properties of the system. This is because the choice of substrate will determine the type of strain in the grown GaAsSb barrier layers (i.e. compressive or tensile) as well as the amount. The residual strain at the surface of the GaAsSb influences the size of the InAs QDs with a greater residual strain seeing smaller dots formed. This has been confirmed for QDs grown on samples with a GaAsSb layer with thickness less than the observed critical thickness of ~ 25nm.

The influence of strain on the QD emission properties has been observed by photoluminescence (PL) [14]. The samples were cooled in a He-flow cryostat to temperatures between 4.4K and 300K. The excitation source was a Ti:sapphire laser with emission wavelength set to 750nm, power density of ~ 28 W/cm^2 and a spot size diameter of approximately 300 μm. The emission was detected through a spectrometer and liquid nitrogen cooled InGaAs detector. As shown in Figure 5, for InAs QDs grown within GaAsSb (Sb 12%) of a buffer of 10nm and therefore lower residual strain. Sample C would be expected to have partially relaxed and so the QDs would be larger then for Samples A and B. The peak for Sample C being at a higher wavelength (lower energy) confirms this.

An even greater influence of strain is seen when time-resolved photoluminescence is used. The excitation pulses were of ~130 fs duration at a repetition rate of 76 MHz and a Hamamatsu C4334 streak camera detected the emission giving a time resolution of the setup of less than 80 ps. As shown in Figure 4, when the results from TRPL are analyzed, the lifetimes for photo-generated carriers is greater in samples B and C. It can be inferred that samples B and C have a type II QD/barrier band structure and the thicknesses of the GaAsSb buffer/cap combination are a major determinant as to the nature of the QD to barrier transitions. So it can be concluded that the thickness of the barrier layers in a quantum dot solar cell must be considered carefully due to the presence of strain.

IMPLICATIONS FOR QD SOLAR CELL DESIGN

All of the results presented so far have been for samples grown on GaAs substrates. As highlighted by the photoluminescence results, the strain distribution in a sample has a significant effect on the observed behavior of the sample. The amount of mismatch as well as the type of mismatch between the substrate and the buffer layer determines not just the morphology of quantum dots grown on the buffer but also the energy levels present in the dots. It stands to reason then that the choice of substrate is in fact a major decision in the design of a quantum dot solar cell.

The impact of the substrate choice can be seen in Figures 5 and 6. The calculations of the band structure were done using the k.p method with the strain between layers taken into account. For comparison, both show the band structure with no strain included. The most immediately noticeable feature is the difference in the band gaps for the GaAsSb layers on GaAs and InP substrates respectively. While the band gap on a GaAs substrate is ~1.25 eV we see that the band gap drops to under 1.0 eV when we grow the same compound on InP. This is due to the grown layer being under compressive strain for a GaAs substrate and under tensile strain for the InP substrate. Since the selection of suitable band gaps is a key step in the design of a quantum dot solar cell the importance of strain is clear.

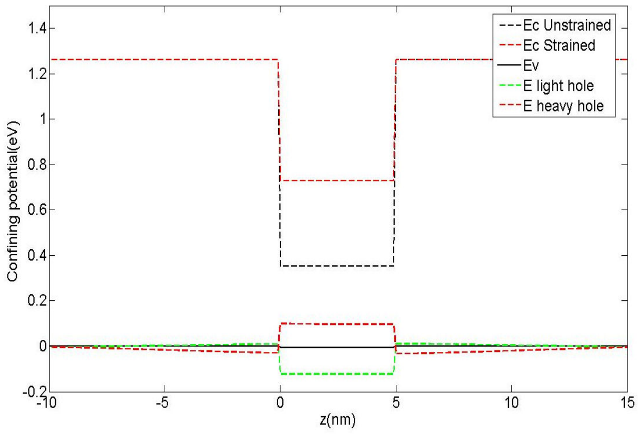

Figure 5: Calculated energy band diagram for InAs on strained $GaAs_{0.88}Sb_{0.12}$ on a GaAs substrate.

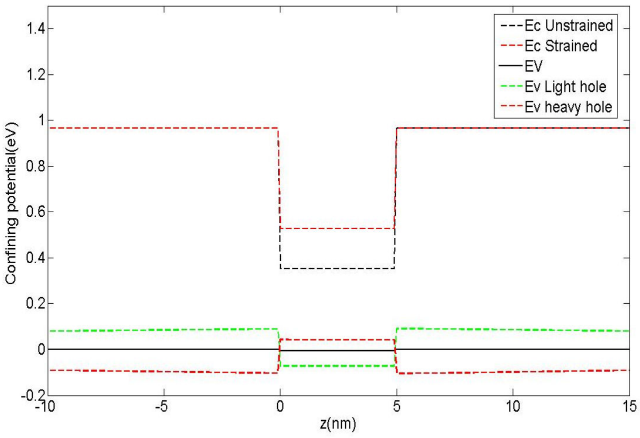

Figure 6: Calculated energy band diagram for InAs on strained $GaAs_{0.88}Sb_{0.12}$ on a InP substrate.

In both cases we see that the confinement energy is reduced in comparison to the unstrained case. This again highlights the importance of taking strain into consideration for the design of quantum dot solar cells since the confinement energy is another key design parameter. The last thing to note is the valence band in the neighborhood of the InAs layer. Neglecting strain we should have a zero offset but with strain we see a splitting in the light hole and heavy hole sub-bands and neither of these show a zero offset. It must be pointed out, however, that the photoluminescence results show that there is a transition from type I to type II meaning that there must be a zero offset for some arrangement.

The final point that must be made is that in order for a quantum dot solar cell to be effective the absorption due to the quantum dots must be significant. This inevitably requires a large number of layers of quantum dots. Once again the strain between layers becomes a key design parameter. In order to avoid relaxation of the grown layers a strain balanced structure needs to be designed. This is the reason for looking at the InP substrate since the GaAsSb layers will be under tensile strain and the InAs layers will be under compressive stress. This alternating of the strain type allows the overall strain to be balanced provided the structure is designed carefully.

The results presented suggest that some adjustments need to be made to the overall design proposed with particular emphasis on the substrate to be grown on. In order to grow barrier layers of the necessary width it may be necessary to investigate the use of metamorphic growth methods in order to tailor the lattice constant to be grown on. Such methods have been successfully used recently to give record breaking efficiency multi-junction solar cells [15].

CONCLUSION

The InAs/GaAsSb QD/barrier material system is being studied as a candidate system for implementation of a QD solar cell using simultaneous multi-color radiative transitions for achieving an efficiency enhancement over a conventional homojunction solar cell. Some of the challenges involved in realizing the QD solar cell in this system have been examined. These include the control of the GaAsSb barrier composition, which has been achieved for variations in flux ratios and temperature. A possible way of enhancing the quantum dot number density by modifying the surface energy was also highlighted. The role of strain has also been discussed, showing the influence of strain on the emission properties of QDs as well as the band structure with evidence of a type I to type II transition shown for variation of GaAsSb buffer/cap combination. The influence of strain must be taken into account when discussing this materials system with the choice of substrate having a large influence on the properties of grown layers. In order to implement the optimum design it may be necessary to employ metamorphic growth methods in order to realize a strain balanced structure.

REFERENCES

[1] A. Luque and A. Marti, “A Metallic Intermediate Band High Efficiency Solar Cell”, *Progress in Photovoltaics: Research and Applications*, 9, p. 73-86, (2001).

[2] A. Luque, and A. Martí, “Increasing the Efficiency of Ideal Solar Cells by Photon Induced Transitions at Intermediate Levels,” *Physical Review Letters*, vol. 78, p. 5014–5017, (1997).

[3] W. Walukiewicz, K.M. Yu, J. Wu, J.W. Ager III, W. Shan, M.A. Scrapulla, O.D. Dubon, and P. Becla, “Highly mismatched alloys for intermediate band solar cells,” *Materials Research Society Symposium Proceedings*, vol. 2005, no. 865, p. 125-130, (2005).

[4] A. Marti, L. Cuadra, and A. Luque, “Partial filling of a quantum dot intermediate band for solar cells,” *IEEE Transactions on Electron Devices*, vol. 48, no. 10, p. 2394-2399, (2001).

[5] W. Shockley, and H.J. Queisser, “Detailed Balance Limit of Efficiency of pn Junction Solar Cells,” *Journal of Applied Physics*, vol. 32, no. 3, p. 510-519, (1961).

[6] I. Gómez, F. Domínguez-Adame, E. Diaz and P. Orellana, “Transport in random quantum dot superlattices,” Journal of Applied Physics, 92(8), p. 4486-4489, (2001).

[7] M.Y. Levy, C. Honsberg, A. Martí, and A. Luque, “Quantum Dot Intermediate Band Solar Cell Material Systems with Negligable Valence Band Offsets,” *Proceedings of the 31st Photovoltaic Specialists Conference, Orlando*, p. 90-93, (2005).

[8] K. Akahane, N. Yamamoto, S. Gozu and N. Ohtani, “Strong photoluminescence and laser operation of InAs quantum dots covered by a GaAsSb strain-reducing layer,” Physica E, 26, p. 395-399, (2205).

[9] K. Yamaguchi and T. Kanto, “Self-assembled InAs quantum dots on GaSb/GaAs(001) layers by molecular beam epitaxy,” *Journal of Crystal Growth* 275, p. 2269-2273 (2005).

[10] R. Kaspi, K. R. Evans, “Sb-surface segregration and the control of compositional abruptness at the GaAsSb/GaAs interface,” Journal of Crystal Growth, 175/176, p. 838-843 (1997).

[11] D. M. Wood and A. Zunger, “Epitaxial effects on coherent phase diagrams of alloys,” Physical Review B, 40(6), p. 4062-4089, (1989).

[12] T. Miura, T. Nakai and K. Yamaguchi, “Atomically-controlled GaSb-termination of GaAs surface and its properties,” Applied Surface Science, 237, 242-245, (2004).

[13] E. Hall, R. Naone, J. E. English, H-R. Blank, J. Champlain and H. Kroemer, “Operational experience with a valved antimony cracker source for use in molecular beam epitaxy,” Journal of Vacuum Science and Technology B, 16(5), 2660-2664, (1998).

[14] A. Pancholi, J. Boyle, V. G. Stoleru and S. P. Bremner, “Effects of strain-reducing Ga(As,Sb) on the Radiative Lifetime of InAs Quantum Dots,” *Applied Physics Letters, to be published*.

[15] R. R. King, D. C. Law, K. M. Edmondson, C. M. Fetzer, G. S. Kinsey, H. Yoon, R. A. Sherif, and N. H. Haram, “40% efficient metamorphic GaInP/GaInAs/Ge multijunction solar cells,” Applied Physics Letters, 90, 183516, (2007).