

GaSb and $\text{Ga}_{1-x}\text{In}_x\text{Sb}$ Thermophotovoltaic Cells using Diffused Junction Technology in Bulk Substrates

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Abstract. This paper presents results of experimental and theoretical research on antimonide- based thermophotovoltaic (TPV) materials and cells. The topics discussed include: growth of large diameter ternary GaInSb bulk crystals, substrate preparation, diffused junction processes, cell fabrication and characterization, and, cell modeling. Ternary GaInSb boules up to 2 inches in diameter have been grown using the vertical Bridgman technique with a novel self solute feeding technique. A single step diffusion process followed by precise etching of the diffused layer has been developed to obtain a diffusion profile appropriate for high efficiency, p-n junction GaSb and GaInSb thermophotovoltaic cells. The optimum junction depth to obtain the highest quantum efficiency and open circuit voltage has been identified based on diffusion lengths (or minority carrier lifetimes), carrier mobility and experimental diffused impurity profiles. Theoretical assessment of the performance of ternary (GaInSb) and binary (GaSb) cells fabricated by Zn diffusion in bulk substrates has been performed using PC-1D one-dimensional computer simulations. Several factors affecting the cell performances such as the effects of emitter doping profile, emitter thickness and recombination mechanisms (Auger, radiative and Shockley-Read-Hall), the advantages of surface passivation and the impact of dark current due to the metallic grid will be discussed. The conditions needed for diffused junction cells on ternary and binary substrates to achieve similar performance to the epitaxially grown lattice- matched quaternary cells are identified.

INTRODUCTION

The availability of bulk substrates of III-V ternary or quaternary substrates with diffused p-n junctions seems to be the most promising option for low cost TPV cell technology. The present work is focused towards evaluating the feasibility of using diffused junctions of bulk GaInSb substrates for TPV cells. A comprehensive analysis of all the issues related to this technology, namely, crystal growth, wafer preparation, diffusion technology, device fabrication, processing and characterization, and, device modeling has been carried out. GaSb has been used as the model baseline material for both experimental and theoretical modeling efforts.

CRYSTAL GROWTH OF GaInSb

Bulk crystals of GaInSb are grown by the vertical Bridgman method from stoichiometric melts [1]. Polycrystalline compound formation was carried out from 6N pure gallium, indium and antimony in an open silica crucible in the presence of eutectic LiCl-KCl salt encapsulation and argon ambient. Synthesized polycrystalline charges were used in subsequent experiments to grow single crystals on $\langle 111 \rangle_B$ or $\langle 100 \rangle$ oriented seeds of compositionally graded GaInSb starting from GaSb or InSb. Unlike binary

CP653, *Thermophotovoltaic Generation of Electricity: 5th Conference*

edited by T. J. Coutts, G. Guazzoni, and J. Luther

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compounds such as GaSb or InSb, growth of ternary alloys still remains a challenge. The major problem in ternary or quaternary alloy growth arises from the wide separation between the liquidus and solidus in the phase diagram [1]. Crystals grown from melt inevitably exhibit mechanical cracks. Furthermore, the alloy concentration changes continuously along the growth direction due to segregation. Hence, no two wafers sliced from two different axial positions in the crystal will have the same composition. In this work, a self-solute feeding method has been developed to grow uniform ternary and quaternary alloys [1]. Crack-free, compositionally homogeneous GaInSb crystals in the band gap range of 0.4 – 0.7 eV have been grown by this method. To describe how the process works, an example of homogeneous $\text{Ga}_{1-x}\text{In}_x\text{Sb}$ growth is presented below.

The growth experiment is initiated with the exact mole fraction of GaSb and InSb as desired in the final crystal. The growth temperature is kept constant at the solidus temperature corresponding to the desired alloy composition (of the crystal). At the growth temperature, the melt composition is decided by the liquidus of the ternary phase diagram. Hence only a fraction of the initial charge is in liquid phase. As solidification proceeds, the liquid gets depleted in the higher melting binary component which is then replenished from the undissolved solute. In the case of GaInSb growth, the solvent is Ga-In-Sb pseudo-binary liquid and the undissolved solute is GaSb. The driving force for solute transport (and growth) is primarily diffusion controlled. This drastically reduces the growth rate of the alloys to ~ 0.1 mm/hr. To enhance the growth rate, a temperature gradient was imposed to increase the solute dissolution rate and the rate at which the solute arrives at the solid-liquid interface. With a temperature gradient of $30^\circ\text{C}/\text{cm}$, maximum growth rate of 1.5 mm/hr for inclusion free crystals could be attained. Figure 1a shows a uniform 2 inch diameter polycrystal of $\text{Ga}_{0.75}\text{In}_{0.25}\text{Sb}$ grown using the self-solute feeding method. A single crystal and a bi-crystal GaInSb grown from InSb and GaSb single crystalline seeds respectively are shown in Figures 1b and 1c, respectively.

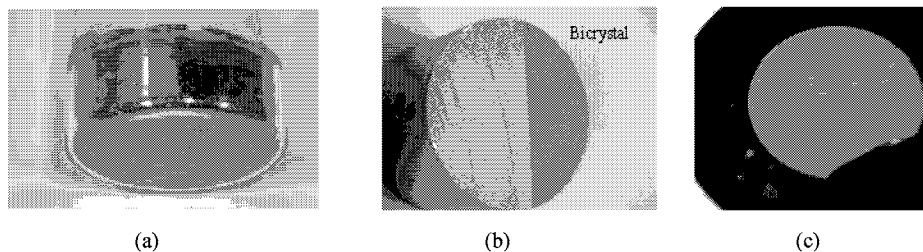


Figure 1 (a) Two inch diameter compositionally homogeneous polycrystal of $\text{Ga}_{0.75}\text{In}_{0.25}\text{Sb}$ grown using the self solute feeding method, (b) Bi- crystal and (c) Single crystal of compositionally graded GaInSb grown from GaSb and InSb single crystalline seeds, respectively.

SUBSTRATE PREPARATION of GaInSb

Ternary alloys are fragile and extreme care is needed when handling during the slicing and polishing of wafers. The as-grown GaInSb boules were sliced either using a single wire saw from Princeton Scientific Company, with a $50\ \mu\text{m}$ thick tungsten wire

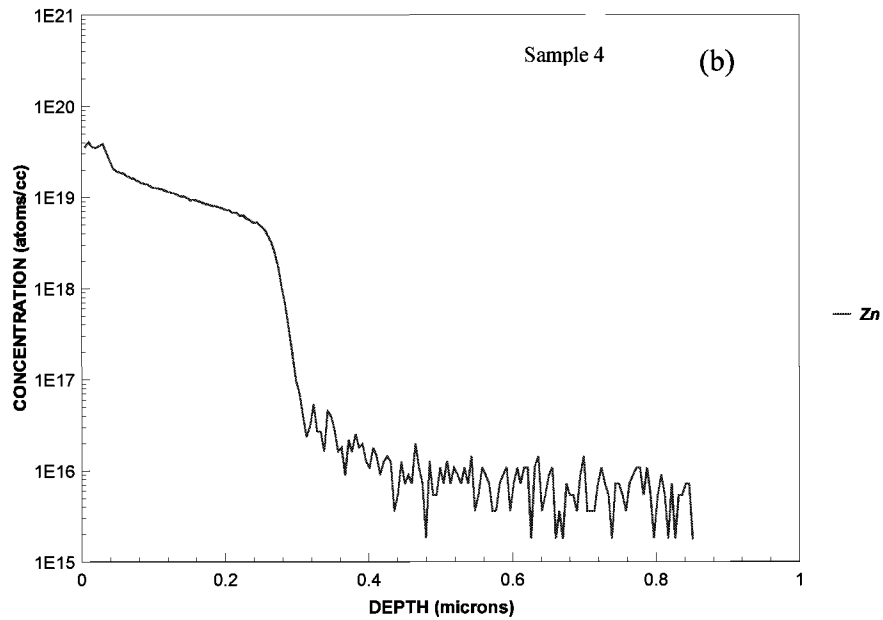
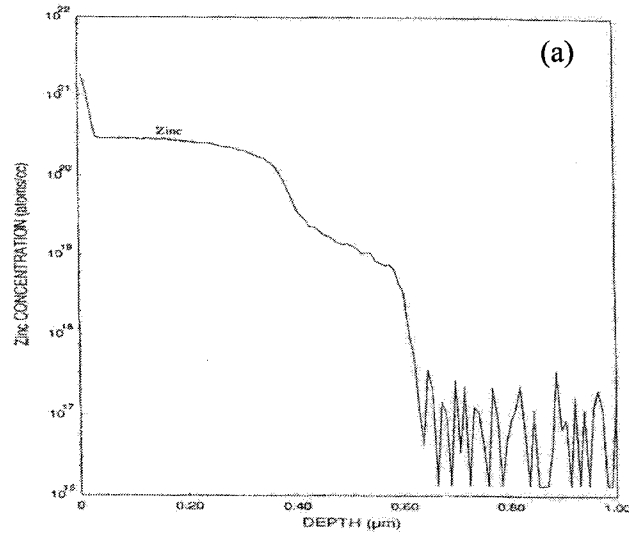
and an abrasive slurry feeder, or a Southbay Technology diamond coated blade saw. For mechanical lapping of ternary substrates, the use of large diameter abrasives ($> 5 \mu\text{m}$) introduces permanent cracks in the wafers. Cracking can be avoided by using smaller abrasive particles ($\sim 1 \mu\text{m}$) for lapping. However, this increases the lapping duration. Prolonged lapping and polishing cycles can also lead to mechanical damage of the wafers. In this work, a novel approach for preparing damage-free GaInSb wafers using the Baikalex CR- series of agglomerate-free alumina slurries has been developed [2]. Rapid removal of material has been evidenced with specific slurries containing abrasive particles of $1 \mu\text{m}$ and less. The high removal rate exhibited by these slurries is attributed to the agglomerate-free nature resulting from special slurry preparation procedures. The final polishing step was done using a soft velvet pad and a high pH (>10) silica slurry (Glanzox) from Southbay Technology that helps in removing the surface contaminants left behind by the alumina slurry. Wafers were finally cleaned in deionized water with scrub and sponges provided by Rippey Corporation. Surface evaluation of the wafers using a Nanospec atomic force microscope (AFM) revealed surface roughness of less than 0.5 nm (in a $10 \mu\text{m} \times 10 \mu\text{m}$ scan area). This is comparable to the best available commercial GaSb wafer surfaces.

Zinc DIFFUSION IN GaSb AND GaInSb

The junction fabrication technology is based on zinc diffusion in n-GaSb and n-GaInSb substrates (Te-doped) [3-6]. The typical zinc profile after a single step diffusion process consists of a heavily doped near-surface region, followed by a plateau and a graded region near the metallurgical junction [3-6]. There are two requirements for obtaining high quantum efficiency and low dark current (and high fill factor). The light absorbing layer should have a low doped concentration for a high minority carrier diffusion length and hence be shallow in depth for high doping concentration (typically the case with a diffused junction emitter). On the other hand, for a good ohmic contact, a heavily doped (for low contact resistivity) and deep junction (to prevent metal spiking from shorting the cell) is required. A high near surface electric fields resulting from diffused impurity profile is advantageous for devices as it reduces the surface recombination velocity for minority carriers (necessary for high quantum efficiency and low dark currents).

In the present work, a single step diffusion and precise emitter etching process has been developed to take advantage of the high near surface electric fields inherent in diffused junctions. For diffusion in GaSb, $\langle 100 \rangle$ oriented n-GaSb commercial wafers from Wafer Tech. Inc. with carrier concentrations of $2 - 4 \times 10^{17} \text{ cm}^{-3}$ were used. For diffusion in GaInSb, polycrystalline or un-oriented single crystalline wafers of n-GaInSb grown in-house with carrier concentrations in the range of $7 \times 10^{17} - 2 \times 10^{18} \text{ cm}^{-3}$ were used. Prior to diffusion, the wafers were degreased in xylene, acetone and methanol, followed by etching the native oxide in HCl. The diffusion was carried out in a pseudo-closed graphite box with the wafer placed above the zinc pellet (approximately 1 cm away). Optimum diffusion temperatures and times have been established for GaSb and GaInSb through post diffusion surface analysis and feedback from device performances (QE, I-V). For GaSb, Zn-diffusion at 500°C for 5 hours seems to be suitable, whereas for

GaInSb in the band gap range of 0.5 – 0.6 eV, 450 °C for 2 hours gave better results. With the above conditions, typical junction depth for GaSb was in the range of 0.6 – 0.8 μm and 0.3 – 0.6 μm for GaInSb depending on alloy composition.



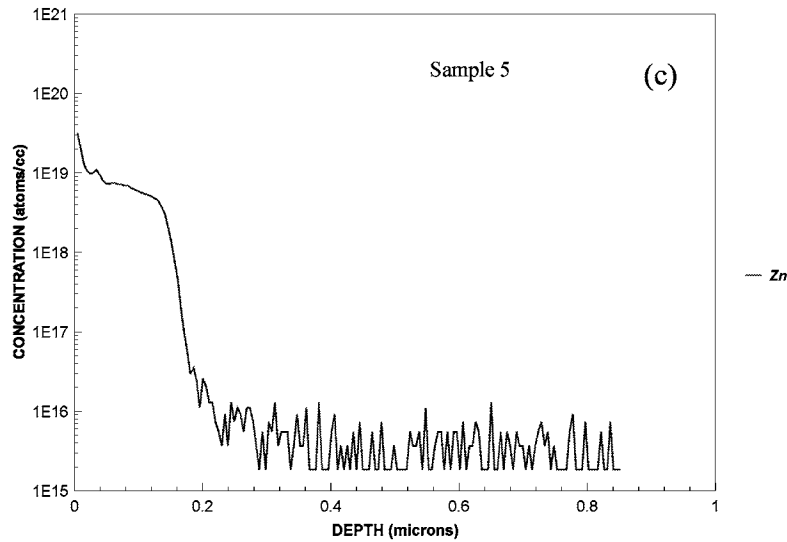


Figure 2. Zinc profiles in n-GaSb diffused at 500 °C for 5 hours (as determined using secondary ion mass spectrometric (SIMS) technique): (a) as-diffused sample, (b) and (c) after etching the diffused sample in ammonium sulphide for 29 min and 55 minutes, respectively.

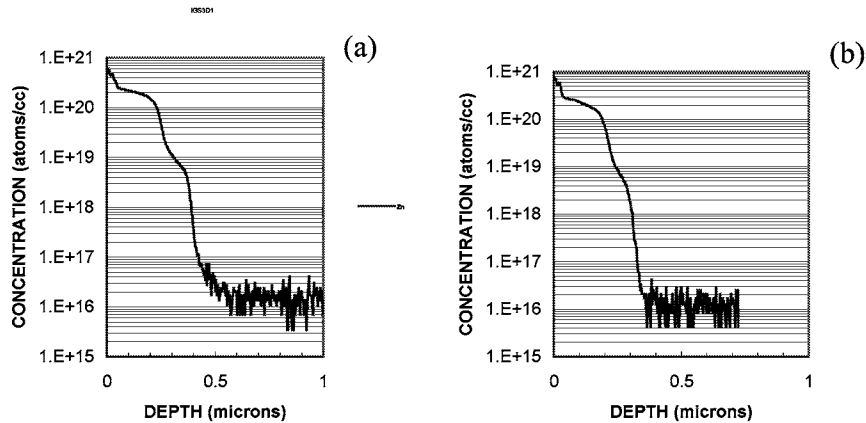


Figure 3. Zinc profiles in as-diffused GaInSb samples of (a) 0.56 eV and (b) 0.6 eV. Both the samples were diffused at 450 °C for 2 hours.

Post diffusion emitter etching for GaSb was performed using ammonium sulphide $[(\text{NH}_4)_2\text{S}_x]$ solution with etching rate close to 0.2 nm/sec. For GaInSb emitter thinning, anodic oxidation was performed using a 3% aqueous solution of tartaric acid in ethylene glycol (1:2 by volume) [5,6]. Figure 2a shows a typical zinc profile in GaSb obtained from secondary ion mass spectrometric (SIMS) measurements. Figures 2b and 2c show

the zinc profiles in the samples after etching in ammonium sulphide. Figures 3a and 3b show the zinc profiles in as-diffused GaInSb with band gaps of 0.56 and 0.6 eV, respectively clearly indicating that the zinc diffusion rate increases with the increase in indium concentration in GaInSb.

To monitor the junction depth during the post diffusion emitter etching, photovoltage measurements were performed using a two-point probe set-up [7]. The diffused sample was placed on a metal block and the top surface was contacted with a metal point probe. A tungsten lamp was used to illuminate the sample and the shift in I-V (the photovoltage) in the low current regime was measured using an oscilloscope. The photovoltage depends on the junction depth and the surface electric field (due to diffused impurity profile). A typical photovoltage profile as a function of cumulative etching times is shown in Figure 4. Initially the photovoltage increases slowly, followed by a rapid increase; beyond the maximum value, the photovoltage decreases drastically until the junction is reached. The maximum photovoltage corresponds to a thin emitter with surface zinc concentration (as in Fig. 2c) an order of magnitude lower than in the as-diffused sample (Fig. 2a). As will be described in the next section, the external QE increases with the decrease in emitter depth, whereas the open circuit voltage (V_{oc}) decreases. Hence it is essential to optimize the junction depth for achieving maximum power output instead of either higher QE or V_{oc} . By comparing the external QE and V_{oc} in the final cells with photovoltage of the etched junction, it has been ascertained that a photovoltage of 100 – 150 mV will result in the best GaSb TPV cell. For the best GaInSb TPV cells, the photovoltage ranged between 20 to 40 mV.

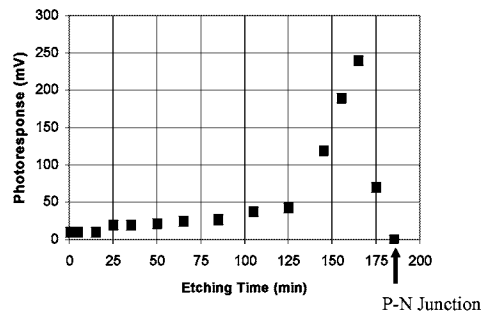


Figure 4. Photovoltage versus etching time for GaSb p-n junction during the emitter thinning process using ammonium sulphide solution

THERMOPHOTOVOLTAIC CELL FABRICATION AND CHARACTERIZATION

The TPV cells fabrication process (such as front and back side metallization, lift-off scheme, mesa etching) and cell characterization schemes were identical to that reported earlier [8]. The quantum efficiencies and I-V characteristics for the two GaSb cells fabricated using the single step diffusion and etching technique (with zinc profiles as shown in Figures 2b and 2c) are shown in Figures 5a and 5b, respectively. The values

of quantum efficiencies and dark currents are amongst the best reported for GaSb TPV cells. It is important to note that there is a one-to-one correlation between the I-V and emitter depth. Even though the external QE are identical for the cells, a thinner junction results in an increase in leakage current (and hence a decrease in open circuit voltage). There is an optimum emitter depth to obtain the highest QE and lowest leakage current. If the emitter is thick, the external QE will decrease due to the high doping concentration in the emitter region which decreases the minority carrier lifetime (see Figure 6a). On the other hand, if it is too thin, the leakage current increases which decreases the V_{oc} (as shown in Figure 6b). The optimum emitter thickness to obtain the highest QE with lowest leakage current is dependent on the zinc profile. With the present single step diffusion profiles and etching technique, the optimum junction depth for the best GaSb cell performance is estimated to be approximately $0.4\ \mu\text{m}$.

Figures 7a and 7b show the external QE and I-V for three polycrystalline GaInSb TPV cells with un-optimized junction depths. Both the external QE and V_{oc} in these cells are comparable to those reported for epitaxial grown cells. These results are quite encouraging. Further improvements in performances may be possible by optimizing the junction depth and the base doping of the substrates.

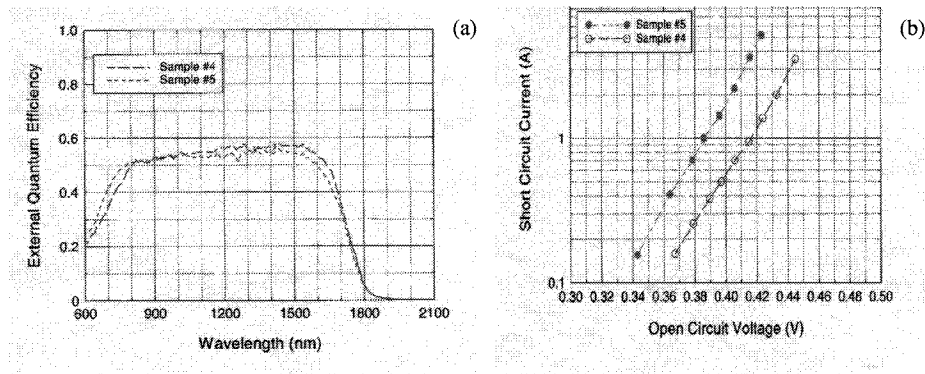


Figure 5. (a) Quantum efficiencies and (b) I-V characteristics of the zinc diffused GaSb TPV cells with diffusion profiles shown in Figs. 2b and 2c (samples 4 and 5, respectively).

MODELING OF Zn DIFFUSED GaSb AND GaInSb TPV CELLS

To complement the experimental part of this study, computer simulations of the Zn diffused GaSb and GaInSb TPV cells were performed. The PC-1D commercial program [9] was used with appropriate material parameters for GaSb and for the GaInSb alloys. Material constants such as energy band parameters, index of refraction, optical absorption coefficients, mobility as a function of the doping concentration are well known for GaSb and they can be extrapolated with a good degree of certainty for the GaInSb alloys [10]. Two parameters that are difficult to obtain accurately for the GaInSb alloys are the Auger recombination coefficient and the band gap narrowing. Values

obtained from recent computer calculations taking into account the non-parabolic nature of the energy bands were used [11].

The Zn doping profile in the emitter, which was obtained from SIMS measurements in the diffused bulk samples, and the base doping which was obtained from Hall measurements on the bulk samples before diffusion were taken into account in the computer simulation. The value of the front surface recombination velocity was chosen so that the simulated external quantum efficiency at 600 nm corresponded to the measured value in the TPV cells with a low doped and thin emitter. The base length of the TPV cells was chosen to be 100 μm so the value of the back surface recombination velocity would not be significant. In addition the metallic grid, covering 10 % of the total cell area, was considered as a parasitic diode with a dark current determined by the metallic grid area, which had a surface recombination velocity equal to the thermal velocity.

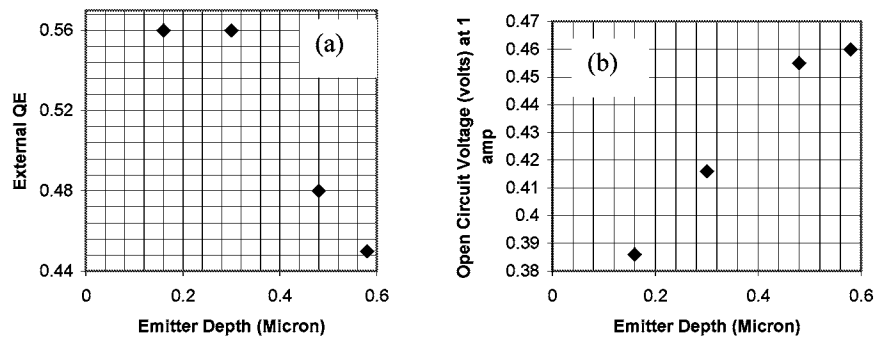


Figure 6. (a) External QE and (b) V_{∞} versus emitter depth for GaSb TPV cells

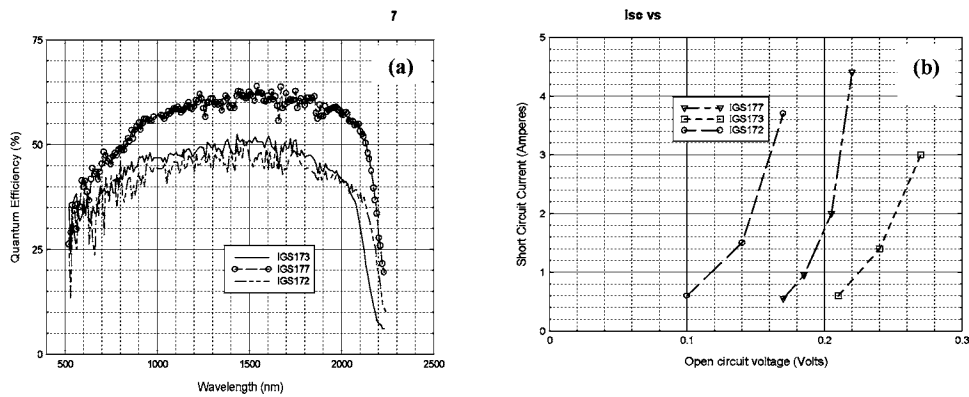


Figure 7. (a) External Quantum Efficiencies and (b) I-V characteristics of the zinc diffused GaInSb TPV cells

Using the SIMS profiles shown previously in Figures 2b and 2c, the performance of GaSb TPV cells with an N- doped base of 3×10^{17} donors/cm³ as a function of junction depth was simulated and the results are shown in Figure 8a and Figure 8b. Figure 8a shows the simulated open circuit voltage as a function of junction depth for a short circuit photocurrent (J_{SC}) of 1 A/cm². Experimental values obtained from fabricated GaSb TPV cells of different junction depths show a very good agreement which validates the simulation results. Figure 8b shows the maximum power output as a function of junction depth. The maximum power is achieved at a junction depth in the range of 0.3 - 0.4 μm . This result is in agreement with the experimental results. The high doping concentration at and near the surface, shown by the SIMS profile, causes a high dark saturation current due to Auger recombination and this high doping region of the Zn diffusion has to be etched away in order to achieve a low dark saturation current. The simulations show that a way to increase the power output is by reducing the front surface recombination velocity. The results indicate that the maximum power output can be increased by approximately 8% by reducing the front surface recombination velocity from 3×10^6 cm/s to 10^3 cm/s. This reduction could be achieved by passivating the GaSb front surface.

Subsequently, computer simulations were performed to obtain an estimate of the optimum junction depth for GaInSb. Using the SIMS profile shown in Figure 3a, the performance of GaInSb TPV cells with band gap of 0.56 eV was simulated. The maximum power output as a function of junction depth is shown in Figure 9. The optimum junction depth for the TPV cell fabricated with 0.56 eV GaInSb with the diffused Zn profile as shown in Figure 3a is around 0.2 microns. The simulations show that the short circuit photocurrent decreases as the junction depth increase since more carriers are photo-generated in the emitter region where they are lost because of the short lifetime and high surface recombination velocity. As in the case of the GaSb TPV cell, the open circuit voltage increases with increase in junction depth up to 0.25 microns beyond which the open circuit voltage decreases slightly. Because of this behavior of the short circuit photocurrent and open circuit voltage, there is a maximum in the output power as function of junction depth.

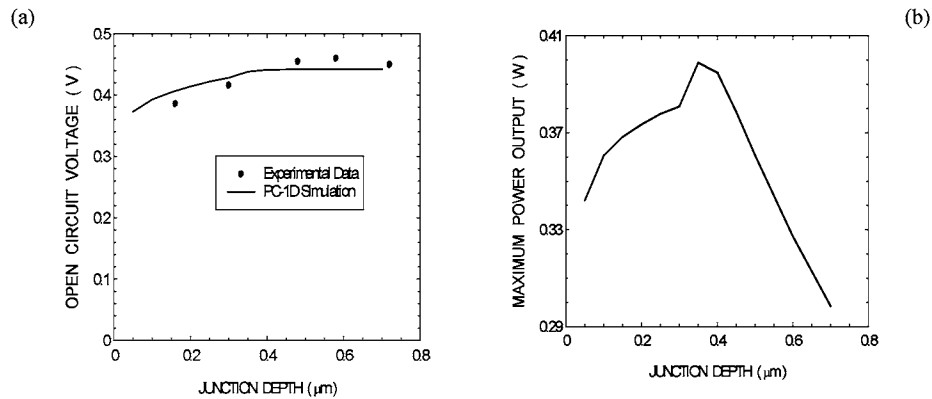


Figure 8. (a) Open Circuit Voltage and (b) Maximum power output as a function of junction depth for Zn-diffused GaSb TPV Cells

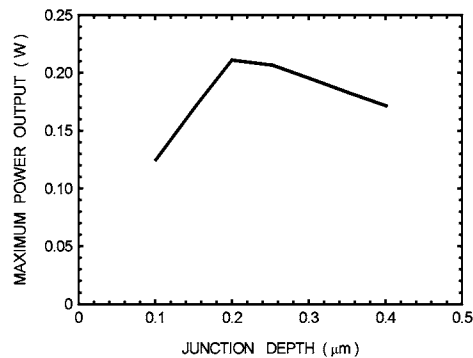


Figure 9. Maximum power output as a function of junction depth for Zn-Diffused GaInSb TPV Cells

CONCLUSION

In summary, we have been able to demonstrate high performance GaSb and GaInSb TPV cells fabricated from bulk substrates by zinc diffusion technology. Peak external quantum efficiencies exceed 50% for GaSb TPV cells and greater than 60% for InGaSb devices. The effect of junction depth on the power output has been studied experimentally as well as by theoretical simulations. Emitter depths in diffused junction cells necessary for maximum power output have been estimated for GaSb and GaInSb.

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