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Low Bandgap GaInAsSbP Pentanary Thermophotovoltaic cells

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Abstract

The liquid phase epitaxial growth of pentanary GaInAsSbP lattice matched onto GaSb and InAs substrates is reported for use in narrow band gap thermophotovoltaic cells. The epitaxial layers were characterized and exhibited intense photoluminescence up to room temperature. Prototype thermophotovoltaic p-i-n diodes were fabricated which were sensitive in the mid-infrared spectral range having cut-off wavelengths in the range 4.0 - 4.5 µm at room temperature.

Key words

Thermophotovoltaic, Liquid Phase Epitaxy, Mid-infrared, III-V Semiconductors, GaInAsSbP

1. Introduction

Thermophotovoltaic (TPV) cells are solid-state *p-n* junction semiconductor devices that directly convert heat into electric power. They absorb the infrared radiation emitted from a hot source and produce electric power by way of the photovoltaic effect. Potential applications include industrial waste heat recovery, domestic combined heat and power generation, hydrogen powered transport and silent or remote power generation [1]**.** Most previous work on TPV devices has concentrated on III-V semiconductors including; Zn-diffused GaSb bulk cells (bandgap 0.7 eV) [2], InGaAs on InP [3] (typically E_g = 0.5-0.73 eV, but which is limited by lattice mismatch to the higher bandgap ranges) and InGaAsSb on GaSb [4] (constrained to E_g = 0.5 eV by a miscibility gap). For thermal emitter temperatures in the range 1000-1500 °C the blackbody spectrum requires an optimum bandgap between 0.3-0.6 eV which is considerably lower than virtually all conventional TPV cells. In this work we report on the liquid phase epitaxial growth of InAsSb/ GaInAsSbP alloys on GaSb and InAs substrates. Our objective is to develop these materials for use in low bandgap TPV cells that could operate with cooler thermal sources around 1000 °C.

2. Experimental Procedures

Liquid phase epitaxy (LPE) is an attractive option for the development of practical TPV cells. The technology is inexpensive and can yield high-quality material with excellent quantum efficiency since growth occurs near thermodynamic equilibrium. Epitaxial growth of $InAs_{1-x}Sb_x$ and $Ga_{1-x}In_xAs_ySb_{1-y-z}P_z$ single epilayers and *p-i-n* homostructures was carried out from antimony-rich melts onto both p-type GaSb (100) and n-type InAs (100) substrates using a conventional horizontal sliding graphite boat in an ultrapure hydrogen atmosphere. The use of antimony as the solvent for LPE growth of GaSb-related alloys avoids substrate erosion and reduces the formation of Sb vacancies [5].Growth melts were prepared from 6N Sb and 7N In pure metals, while the the sources of Ga, As and P were undoped polycrystalline GaSb, InAs and InP binary compounds. Growth was implemented from supercooled melts at temperatures within the interval 585-600 °C. The thickness of the resulting layer epilayers was in the range 1.0-3.5 µm when using a crystallization rate of 4-7 µm per minute and a super-cooling ΔT in the range 8-15 °C [6].

The resulting layers were characterized using high resolution X-ray diffraction, scanning electron microscopy and photoluminescence (PL). The composition of the layers was measured using energy dispersive X-ray microanalysis (EDAX). The *p-i-n* structures were processed into 1 mm diameter mesa-etched diodes using conventional photolithography and processing techniques. Ohmic contacts were formed by thermal evaporation of gold and the resulting chips were mounted onto TO-46 headers for testing. A Keithley 2400LV source meter was used for current-voltage (I-V) measurements in the dark and under illumination. A tungsten halogen lamp was used as a light source which provided an incident power of approximately 500 mW/cm^2. The spectral response was measured with a grating monochromator (blazed at 3.5 µm) and lock-in amplifier using a chopper frequency of 180 Hz and a blackbody temperature of 1100 K.

3. Results and Discussion

A. LPE Growth on GaSb substrates

The power dependent photoluminescence emission spectra of undoped $InAs_{0.91}Sb_{0.09}$ grown lattice matched onto GaSb is shown in figure 1. Two emission bands can be observed with peak energies of 316 meV (3.91 µm) and 326 meV (3.79 µm) which are associated with conduction band to acceptor recombination. The 4 K bandgap of $InAs_{0.91}Sb_{0.09}$ is 335 meV which yields acceptor activation energies of 19 and 9 meV respectively. Emission is obtained from the deepest levels at low excitation. As the excitation is increased, these saturate and emission is obtained from the shallower acceptor states. At higher temperatures (80 K)

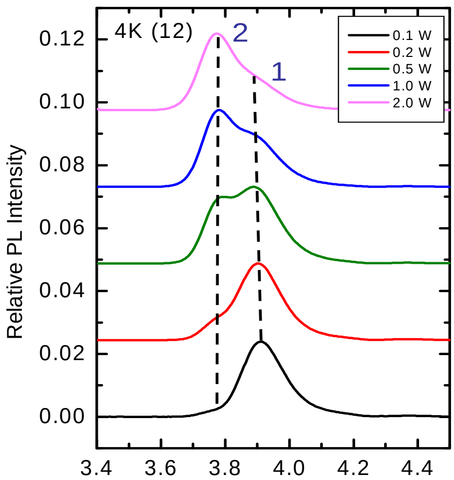


Figure 1: 4 K PL spectrum from InAsSb grown on GaSb. Peaks 1 and 2 correspond to conduction band to acceptor recombination

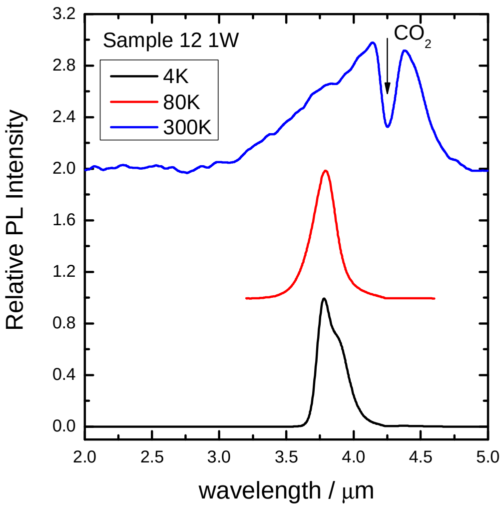


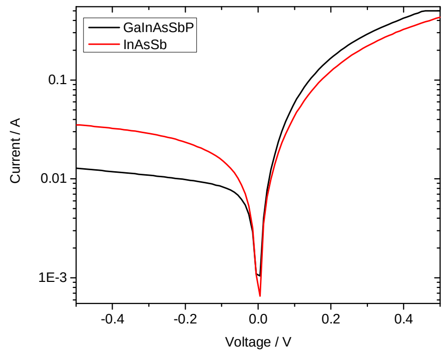
Figure 2: PL spectrum measured at temperatures of 4, 80 and 300 K, showing the CO_2 absorption in the spectrum at 300 K.

recombination from the acceptor levels becomes saturated and band to band recombination is observed. PL was readily obtained up to room temperature as shown in figure 2.

Typical current–voltage (I-V) curves of a p-i-n/P InAsSb/GaSb device measured at room temperature are shown in figure 3. The I-V characteristics can be fitted using the following relationship

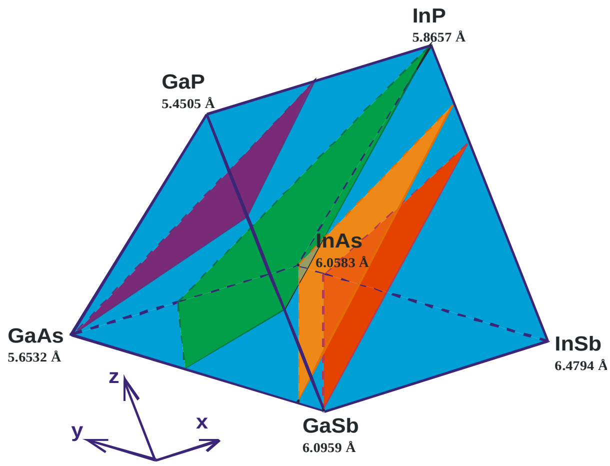
$$I = I_{ph} - \frac{V + IR_s}{R_{sh}} - I_0 \left(e^{\left(\frac{V+IR}{nV_{th}}\right)} - 1 \right) \quad (1)$$

which can be solved by rewriting in terms of the Lambert W function [7]. The parameters I_{ph}, I_0, R_s, R_{sh}, and n represent the photocurrent, reverse saturation current,

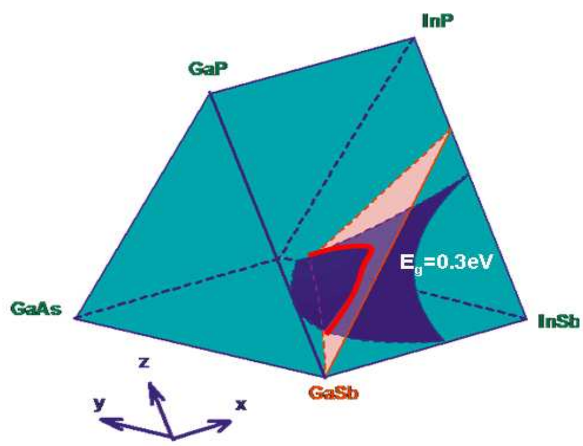


	I_0 (mA)	I_{ph} (mA)	R_s (Ω)	R_{sh} (Ω)	*n*
InAsSb	11	2	0.82	19.1	1.6
GaInAsSbP	7	0.6	0.69	87.8	1.1

Figure 3: Current-voltage characteristics for the 1mm p-i-n/P GaInAsSbP and InAsSb diodes. The table lists the corresponding diode fitting parameters obtained.



(a)



(b)

Figure. 4 (a) Isoperiodic surfaces with different binaries inside the concentration prism of GaInAsPSb. (b) Isoperiodic (pink) with GaSb (a=6.095 Å) and iso-energy (blue) surfaces (Eg=0.3eV) inside the concentration prism of GaInAsPSb.

series resistance, shunt resistance and diode ideality factor, and are given in the table in figure 3

To improve the device characteristics it is necessary to produce material with superior crystalline quality containing fewer defects and dislocations to reduce leakage current and improve both the series and shunt resistance. For $InAs_{1-x}Sb_x$ the associated thermodynamics restricts the epitaxial growth to a relatively narrow growth window < ± 2 ˚C at 560 ˚C. This can be overcome using the pentanary alloy $Ga_{1x}In_xAs_ySb_{1-y-z}P_z$ for which a wider growth temperature window exists ~15 ˚C, enabling more reproducible growth and further material optimization. In fact GaInAsPSb can be grown lattice matched to GaSb, InAs, InP and GaAs [8] (Fig. 4a). It is well known that only one lattice parameter (a_0) and one band gap value (E_g) correspond to a given composition of any ternary alloy. For quaternary materials one can vary the band gap value at a fixed lattice parameter. In the case of pentanary alloys, many compositions with identical band gaps and lattice parameters exist. These form iso-energy and isoperiodic surfaces in the concentration prism. The line (marked in red) in Fig. 4b shows where the iso-energy and isoperiodic lines intersect and determines the alloy with the selected bandgap (0.3 eV in this case). The corresponding alloy compositions can be chosen by moving along this line. Clearly, the additional degree of freedom provides control of material electro-physical properties by changing its chemical composition whilst maintaining a fixed band gap. At a fixed band gap value and lattice parameter, the spin-orbit splitting value, refractive index, thermal expansion coefficient and many other parameters of the pentenary alloy could be changed.

Temperature dependent PL emission spectra from a single $Ga_{0.03}In_{0.97}As_{0.81}P_{0.06}Sb_{0.13}$ pentanary epilayer are shown in figure 5, where a single peak is observed throughout the whole temperature range. The resulting temperature dependence of this peak is shown in figure 6. A small blue shift is observed at low temperatures before the peak shifts to longer wavelengths. The solid line shows the resulting fit using the Varshni equation [9].

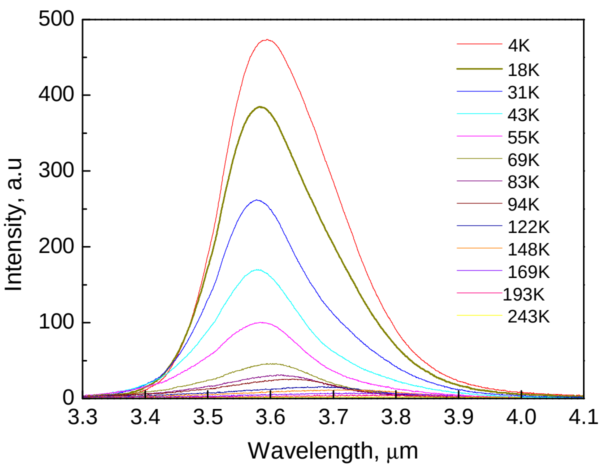


Figure 5: Temperature dependence of PL spectra for $Ga_{0.03}In_{0.97}As_{0.81}P_{0.06}Sb_{0.13}$epilayer.

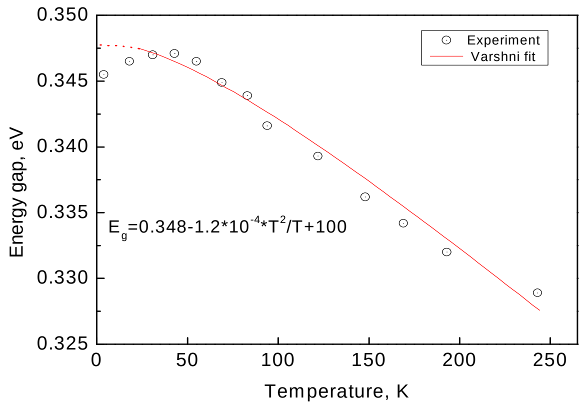


Figure.6: Energy gap variation with temperature for $Ga_{0.03}In_{0.97}As_{0.84}P_{0.05}Sb_{0.11}$ alloy.

$$E_g(T)=E_g(0) - \alpha T^2/(T+\beta) \quad (2)$$

where $E_g(0)$ is the energy gap at 0 K, and α and β are materials constants. Values of 0.348 eV, 1.2 × 10^{-4} eV/K and 100 K were found for $E_g(0)$, α and β respectively. The S-shaped curve is characteristic of recombination through localized states near the band edges and has been previously observed in GaInAsSbP and AlGaAsSb alloys [10, 11].

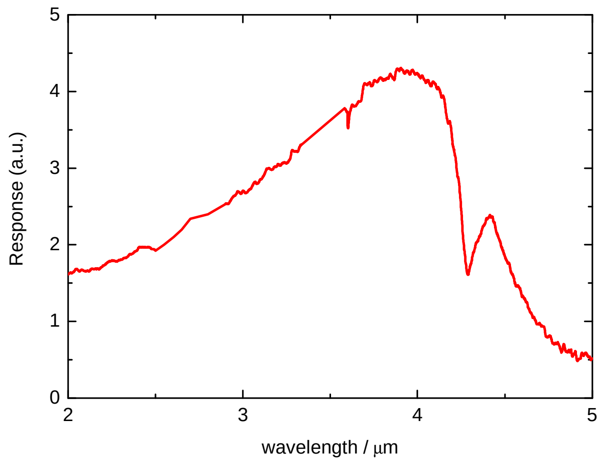


Figure 7: Spectral Response of the p-i-n/P GaInAsSbP TPV diode measured at 300 K.

The resulting I-V plot obtained from a 1 mm p-i-n/P GaInAsSbP p-i-n diode is shown in figure 3 (black line) where the leakage current is reduced compared to InAsSb and an ideality factor closer to one is obtained. The corrected spectral response obtained from this prototype TPV diode at room temperature is shown in figure 7. The cut-off wavelength occurs near 4.5 µm just beyond the characteristic absorption from CO_2 present in the lab atmosphere which is observed at 4.2 µm.

B. LPE Growth on InAs substrates

With reference to figure 4, GaInAsSbP can also be grown lattice-matched to InAs. After some investigation of growth parameters we successfully produced good quality epitaxial layers of $Ga_{0.04}In_{0.96}As_{0.82}Sb_{0.14}P_{0.04}$ on InAs (100) substrates. These layers were characterised in the same manner as those grown on GaSb and the results have been reported in our earlier publication [12] From this alloy composition we obtained a wider bandgap of 0.324 eV corresponding to 3.7 µm at room temperature. Heterojunction TPV diodes were subsequently fabricated by growing a wider band gap p^+ $InAs_{0.62}Sb_{0.14}P_{0.24}$ quaternary layer above the undoped pentanary GaInAsSbP layer. The quaternary wide gap layer is optically transparent, which improves transmission, minimises photo-generation in the surface layer and reduces minority carrier recombination into the active region [13]. The current–voltage (I-V) curve from one of the devices measured at room temperature is shown in figure 8. The characteristics are similar to the previous devices grown on GaSb substrates but with a sharper turn-on voltage at 0.1 V. The expanded I-V characteristic using 1100 K black body illumination is shown in figure 9.

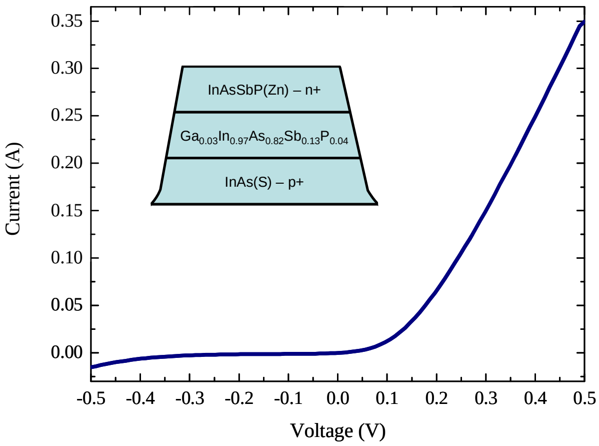


Figure 8: Current-voltage (I-V) curve for P-i/N InAsSbP-GaInAsSbP-InAs TPV diode measured at 300 K. (Inset Schematic structure of the single heterojunction pentanary diode.)

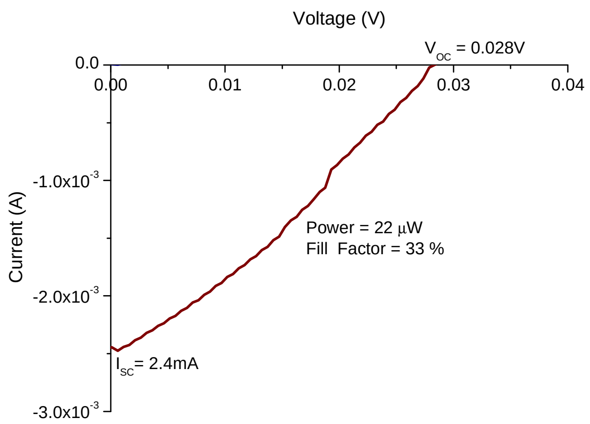


Figure 9: Expanded current-voltage (I-V) curve for P-i/N InAsSbP-GaInAsSbP-InAs diode under illumination by a halogen lamp ~500mW/cm^2, measured at 300 K.

An open circuit voltage of 0.028 V, a short-circuit current of 2.4 mA, was obtained with 500mW/cm^2 illumination intensity, producing a maximum output power of 22 µW and with a corresponding fill factor of 33%. It should be stressed that these values can be much improved since the devices are far from optimized with respect to the active region thickness, the doping concentrations or the cell architecture.

The temperature dependent photo-response is shown in figure 10. The 100 K absorption spectrum peaks at 2.75 µm (labelled I) and displayed a long wavelength shoulder at ~3 µm. At higher temperatures the absorption due to peak I decreased and red-shifted. At 170 K a second peak (labelled II) at 3.16 µm became

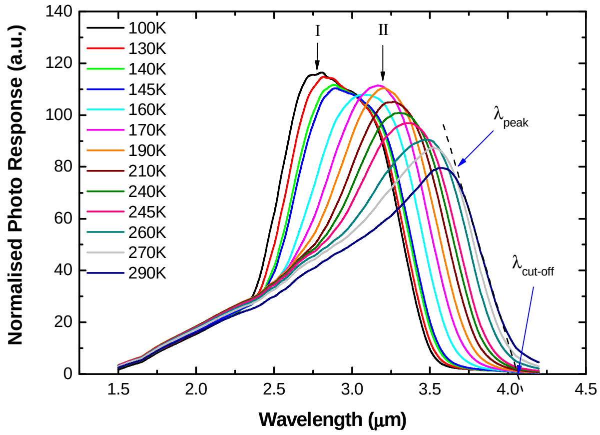


Figure 10: Temperature dependent photo-response for P-i/N InAsSbP-GaInAsSbP-InAs device. The separate absorption peaks I and II are shown with the peak and cut-off wavelengths labelled.

dominant. The absorption of peak II then decreased and red shifted to 3.57 µm as the temperature increased to 290 K. Consequently, peak I may be attributed to absorption in the $InAs_{0.62}Sb_{0.14}P_{0.24}$ window layer which has a band gap of ~0.44 eV (2.8 µm) at 160 K. Peak II arises from absorption in the pentanary $Ga_{0.04}In_{0.96}As_{0.82}Sb_{0.14}P_{0.04}$ active later material. The changes in behaviour of the spectral response can be mainly attributed to the decrease in the photo-generated minority carrier diffusion length in the quaternary alloy with increasing temperature. Near room temperature fewer electron-hole pairs generated in the p^+ $InAs_{0.62}Sb_{0.14}P_{0.24}$ layer are unable to diffuse across the window layer without recombining. As such, only electron-hole pairs generated in the $Ga_{0.04}In_{0.96}As_{0.82}Sb_{0.14}P_{0.04}$ layer (peak II) contribute to the TPV signal at high temperatures.

4. Conclusion

In summary, we have demonstrated the LPE growth of InAsSb and GaInAsSbP alloys lattice matched onto GaSb and InAs substrates which exhibit bright photoluminescence up to room temperature. Prototype thermophotovoltaic (TPV) diodes based on $InAs_{0.91}Sb_{0.09}$ and $Ga_{0.02}In_{0.98}As_{0.84}P_{0.02}Sb_{0.14}$ *p-i-n* structures were fabricated and demonstrated. We found that the pentanary alloy was of a higher crystalline quality and exhibited superior diode characteristics. $Ga_{0.04}In_{0.96}As_{0.82}Sb_{0.14}P_{0.04}$ alloys grown on InAs were also realised and further improvements were obtained by utilizing a InAsSbP/GaInAsSbP heterojunction. The results demonstrate that LPE growth of pentanary alloys of GaInAsSbP with appropriate compositions can provide narrow band gap materials which could offer a possible route to the fabrication of novel TPV cells for electricity generation from waste heat. Further work is required to investigate intrinsic defects in these materials to improve the diode turn-on voltage and to optimise the cell architecture.

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