GROWTH AND INVESTIGATION OF INDIUM ARSENIDE–BASED DIODE HETEROSTRUCTURES FOR MID–INFRARED APPLICATION

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1. Introduction

Photovoltaic devices developed for most thermophotovoltaic (TPV) applications have bandgaps ranging from 0.5eV to 0.75eV. Most works on TPV devices has concentrated on III–V semiconductors InGaAs on InP (typically $E_g = 0.5–0.73$ eV, but limited by lattice mismatch to the high bandgap ranges) [1], or InGaAsSb on GaSb (limited to $E_g > 0.5$ eV by the miscibility gap) [2]. Although III–V ternary and quaternary semiconductors have widely tunable spectral responses, miscibility gaps and lattice mismatch constraints limit the practical range of bandgaps in most of these systems. System modeling results have indicated the advantages of still lower bandgap (< 0.5 eV) TPV cells [3, 4]. A maximum efficiency and maximum power density can be achieved with bandgaps between 0.2–0.5 eV for black body sources temperature in the range of $120^0$K to $250^0$K. This bandgaps range is considerably lower than almost all conventional TPV cells. Thus, there is a need for significant development in both new materials used for TPVs and in processing, to produce high performance TPV converters with lower bandgaps. An alternative to InGaAs on InP and InGaAsSb on GaSb-substrate are less developed epitaxial InAsSbP lattice–matched structures on InAs or GaSb substrates [5-7]. Lattice-matched InAs/InAsSbP TPV cells have variable bandgaps ranging from 0.3 to 0.5 eV, that displace the spectral response to the long-wavelength range, which is impossible to cover by GaSb-based materials.

2. Device structures and growth technique

This report describes our efforts to fabricate lattice-matched p-InAsSbP/n-InAs and p-InAsSbP/n-InAsSbP/n-InAs epitaxial diode heterostructures for TPV converter applications. A new version of liquid–phase electroepitaxy (LPEE) [8] and step–cooling LPE have been employed.

In LPEE technique we used a growth cell consisting of the growth solution and two separate liquid–sources of grown layer components. The control of the growth solution composition, and hence the composition of the grown layer is performed by an electric current–induced electrotransport of each individual component from liquid-sources to the growth solution. The amount of individual solute elements supplying the growth solution is controlled by the duration and strength of the electric current passing through the growth solution and each of two
liquid−sources. This version of LPEE was realized in a horizontal liquid−phase electroepitaxial reactor equipped with a specially modified slider type boat to permit the usage of two additional channels and reservoirs for liquid-source solutions under a Pd-diffused H₂ flow. The epitaxial growth of InAsSbP quaternary layers was performed on n-InAs (100) substrates at a constant temperature and electric current. The growth temperature was varied from 550°C to 580°C at the electric current density in the range of 2 – 4 A/cm². LPEE technique due to the flexible and precision current control of supersaturation in the vicinity of the substrate provides quasi-equilibrium growth conditions and perfect quality of grown layers. Liquidus compositions in equilibrium with InAs₁₋ₓ₋ₐSbxPy solid lattice−matched to InAs substrate (y = 2.23x) were calculated, using a simple solution model for the liquid and a strictly regular solution model for the solid. Using step-cooling LPE and LPEE techniques, we have grown InAs₁₋ₓ₋ₐSbxPy epitaxial layers of different compositions from y=0.04 to y=0.2. The starting point of liquid phase composition for the InAs₁₋ₓ₋ₐSbxPy epitaxial layers growth was determined by the phase diagram simulation. These techniques provide a constant composition along the grown epitaxial layer. For the growth solution formation the 7Ni indium, 6N antimony, undoped InAs and InP crystals were used. The background carrier concentration in undoped InAsSbP n-type layers was n ~10¹⁷ cm⁻³. The p-InAsSbP layers (p~10¹⁸cm⁻³) were grown from the Zn-doped growth solution. For these layers epitaxy step-cooling LPE technique was also performed at 550°C – 580°C during 30 min from 7 – 10°C super-saturated solution. The thickness of epilayers grown by LPE and LPEE was 3 – 5 μm.

The investigations of cross-sectional area of p−n heterojunctions, morphology of layer surface and InAsSbP alloys composition have been carried out using SEM-EDX equipment. A Scanning Electron Microscope “Zeiss DSM 962” equipped with an Oxford Instrument EDX was used for surface imaging and microanalysis (Fig. 1). The results of these investigations have shown that InAs₁₋ₓ₋ₐSbxPy epitaxial films had very smooth, uniform, and mirror-like surface. The etch−pit density on layers surface (N₀ ~10⁴ cm⁻²) was no more than in the InAs substrate. The measurements of lattice mismatch between the InAs substrate and InAs₁₋ₓ₋ₐSbxPy (x=0.08; y=0.14) epitaxial layer as well as the investigations of diode heterostructures interface crystallographic quality have been carried out using X-Ray and TEM equipments. The X-ray bare rocking curves in logarithmic scale and grown heterostructure cross-sectional TEM image are presented in Fig. 2. The investigations showed that the lattice mismatch ratio (∆a/a) ranges from a few 10⁻⁴. The results of TEM measurements show that p-InAsSbP/n-InAs diode heterostructure interface is free of misfit dislocations. About one micrometer above that interface is a network of inplane misfit dislocations that don’t thread up into the epitaxial layer.
Fig. 1. The imaging of InAs substrate and InAs$_{1-x-y}$Sb$_x$P$_y$ ($x=0.04; y=0.08$) epilayer surface and X-ray lines of quaternary epilayer components.

This region is very clean and the dislocations density is too low to measure by cross-sectional TEM.

In order to determine the underlying physics of the p-InAsSbP/n-InAs p-n junction the current-voltage characteristics were measured at different temperatures (from $+20^\circ$C to $-20^\circ$C). The results of current–voltage measurements have shown that an ideality factor is close to 1. Thus, we can conclude at first that n-InAs/p-InAsPSb diode structure has a good quality and at second that the diffusion mechanism is predominant up to $-20^\circ$C. In spite of the fact that the energy band gap of InAsPSb layer is close to InAs substrate band gap a sufficiently high value of the contact potential $V_k$ is observed. The current–voltage measurements have shown that the p-InAsSbP/n-InAs TPV diode structures with higher bandgap of epilayer had more high value of $V_k$. The calculations of the p–n junction saturation current ($I_s$) were carried out to compare experimental results with the theoretically expected. For our n-InAs/p-InAsPSb diode heterostructures at room temperature $I_s = 29 \times 10^{-2}$A/cm$^2$ which is very close to the theoretically expected ($I_s = 15.5 \times 10^{-2}$A/cm$^2$) that testifies to high performance of grown TPV structures.
Fig. 2. The X-ray bare rocking curves in logarithmic scale and cross-sectional TEM image of n-InAs/InAs\(_{1-x-y}\)Sb\(_x\)P\(_y\) (x=0.08; y=0.14) TPV cell.

For the optical response and PL spectra measurements a diode meza-chip with an active diameters of 0.4 - 0.5 mm corresponding to TPV cell standard single segment has been formed. The relative optical response and PL spectra of n-InAs/InAs\(_{1-x-y}\)Sb\(_x\)P\(_y\) (x=0.08; y=0.14) TPV cell are presented in Fig. 3.

**3. Conclusion**

Thus, this report describes our efforts to fabricate lattice-matched p-InAsSbP/n-InAs epitaxial diode heterostructures for TPV converter applications. New versions of liquid–phase electroepitaxy and step–cooling LPE techniques have been employed. The investigations of cross-sectional area of p-n heterojunctions, morphology of layers surface, calculations of quaternary InAsSbP alloys composition and measurements of lattice mismatch ratio have been
carried out using SEM-EDX, X-ray and TEM equipments. Epitaxial structures had a uniform thickness, mirror-like surface and very flat interface.

![Graph showing spectral response and PL spectra of n-InAs/InAs$_{1-x-y}$Sb$_x$P$_y$ (x=0.08; y=0.14) TPV cell.](image)

Fig. 3. The spectral response and PL spectra of n-InAs/InAs$_{1-x-y}$Sb$_x$P$_y$ (x=0.08; y=0.14) TPV cell.

The current–voltage characteristics, spectral response, PL spectra, and other physical parameters of grown diode heterostructures have been investigated. According to our results, we believe that InAsSbP-based epitaxial diode heterostructures and devices are very attractive for TPV applications in low-temperature (less than 1200K) emitters, as well as for other applications in the MID-infrared region.

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REFERENCES