Extending the Cutoff Wavelength of Lattice-Matched GaInAsSb/GaSb Thermophotovoltaic Devices

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Abstract. This paper reports the growth, materials characterization, and device performance of lattice-matched GaInAsSb/GaSb thermophotovoltaic (TPV) devices with cutoff wavelength extended from 2.3 to 2.5 μm. GaInAsSb epilayers were grown lattice matched to GaSb substrates by organometallic vapor phase epitaxy using all organometallic precursors including triethylgallium, trimethylindium, tertiarybutylarsine, and trimethylantimony with diethyltellurium and dimethylzinc as the n- and p-type dopants, respectively. The growth temperature was 525°C. Although these alloys are metastable, a mirror-like surface morphology and room-temperature photoluminescence (PL) are obtained for alloys with PL peak emission at room temperature as long as 2.5 μm. Lattice-matched GaInAsSb/GaSb TPV devices exhibit internal quantum efficiency as high as 90% for devices with a cutoff wavelength of 2.5 μm. The open circuit voltage for extended wavelength devices is 239 mV at 3.6 A/cm^2.

INTRODUCTION

$Ga_{1-x}In_xAs_ySb_{1-y}$ alloys are of interest for lattice-matched thermophotovoltaic (TPV) devices because of the high performance attainable at 2.3 μm [1]. Extension of the TPV device cutoff wavelength λ_c to beyond this wavelength is especially desirable since the emissive power of the radiator is significant at these longer wavelengths, and higher power density can be attained [2]. However, the $Ga_{1-x}In_xAs_ySb_{1-y}$ quaternary alloy system exhibits a miscibility gap [3] in the wavelength range of interest. Thus, to increase λ_c requires the growth of high quality alloys that penetrate further into the miscibility gap. The growth has been difficult because these alloy compositions are metastable, and consequently, no devices with $\lambda_c > 2.3$ μm have been demonstrated previously.

In this paper, the successful preparation of $Ga_{1-x}In_xAs_ySb_{1-y}$ alloys for TPV devices with extended λ_c is reported. Epitaxial $Ga_{1-x}In_xAs_ySb_{1-y}$ layers of various composition, and thus λ_c, were grown lattice matched to GaSb substrates by

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organometallic vapor phase epitaxy (OMVPE). The materials properties are presented for epilayers with increasing x and y values, and thus λ_c varying from 2 to 2.5 μm. High optical quality is achieved for alloys with room-temperature photoluminescence (PL) peak emission at 2.5 μm, and the first demonstration of TPV devices with λ_c out to 2.5 μm is reported.

EPITAXIAL GROWTH AND CHARACTERIZATION

$Ga_{1-x}In_xAs_ySb_{1-y}$ epilayers were grown in a vertical rotating-disk reactor with H_2 carrier gas at a flow rate of 10 slpm, reactor pressure of 150 Torr, and a typical rotation rate of 100 rpm [4]. Solution trimethylindium, triethylgallium, tertiarybutylarsine, and trimethylantimony were used as organometallic precursors. Diethyltellurium (10 ppm in H_2) and dimethylzinc (1000 ppm in H_2) were used as n- and p-type doping sources, respectively. For lattice-matched epilayers, $Ga_{1-x}In_xAs_ySb_{1-y}$ was grown on (001) Te-doped GaSb substrates misoriented 6° toward (111)B. The growth temperature was 525°C.

The surface morphology was examined using Nomarski contrast microscopy and atomic force microscopy (AFM) in the tapping mode. High-resolution x-ray diffraction (HRXRD) was used to measure the degree of lattice mismatch to GaSb substrates. PL was measured at 4 and 300 K using a PbS detector. The In and As contents of $Ga_{1-x}In_xAs_ySb_{1-y}$ epilayers were determined from the combination of 1) HRXRD splitting of ω-2Θ scans; 2) peak emission in 300 K PL spectra; and 3) energy gap dependence on composition, $E(x,y) = 0.726 - 0.961x - 0.501y + 0.08xy + 0.415x^2 + 1.2y^2 + 0.021x^2y - 0.62xy^2$, where $y = 0.867x/(1 - 0.048x)$ for alloys lattice matched to GaSb substrates. For electrical characterization, GaInAsSb was grown on semi-insulating (001) GaAs substrates misoriented 6° toward (111)B. Because of the lattice mismatch between the epilayer and the substrate, a 0.4-μm-thick GaSb buffer layer was grown [4]. Carrier concentration and mobility of GaInAsSb epilayers, which were grown about 3 μm thick, were obtained from Hall measurements based on the van der Pauw method.

GROWTH RESULTS

$Ga_{1-x}In_xAs_ySb_{1-y}$ epilayers of various x and y values were grown lattice matched to GaSb substrates. Figure 1 shows the surface topography of four layers, each about 2 μm in thickness, as imaged by AFM. The In and As concentrations were varied with $0.09 < x < 0.23$ and $0.08 < y < 0.20$. These compositions correspond to values that are predicted to be thermodynamically metastable at a growth temperature of 525°C [3], with higher x and y values more metastable. The AFM images of Figs. 1a – 1c reveal periodic surface features that are oriented perpendicular to the substrate misorientation direction, which is suggestive of bunched supersteps. On the other hand, the irregular features observed for the sample in Fig. 1d imply a three-dimensional growth mode, which is unfavorable.

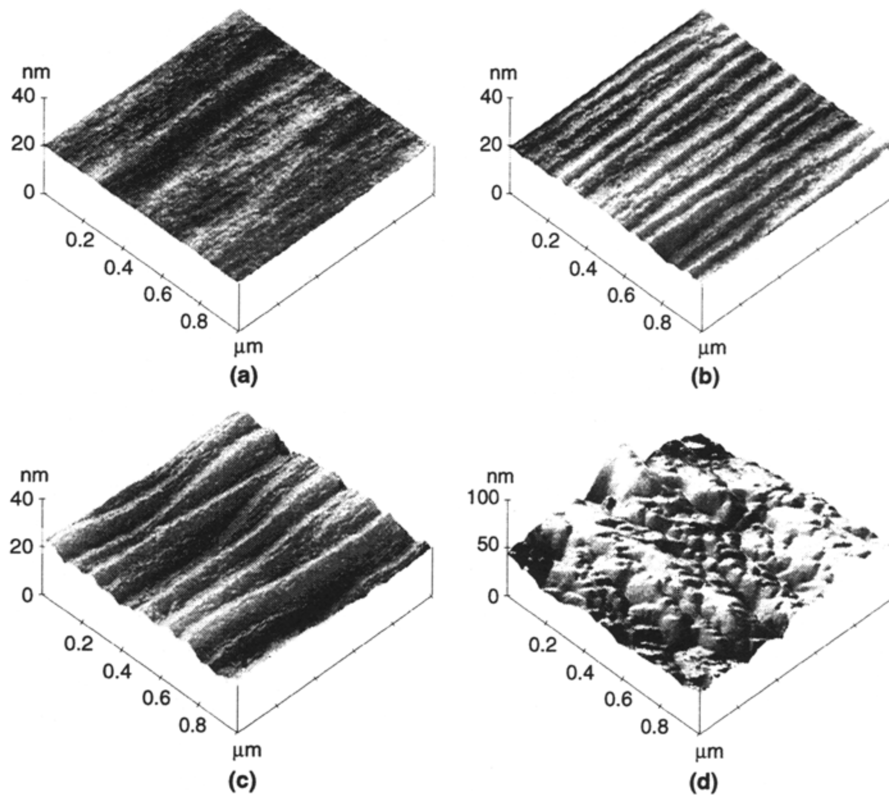

FIGURE 1. Atomic force microscopy images showing surface topography of nominally lattice-matched $Ga_{1-x}In_xAs_ySb_{1-y}$ epilayers grown at 525°C on (001) 6° toward (111)B GaSb substrates. The composition of the layers is: (a) $x = 0.09$, $y = 0.08$; (b) $x = 0.16$, $y = 0.15$; (c) $x = 0.20$, $y = 0.18$; and (d) $x \sim 0.23$, $y \sim 0.21$. The values for the layer shown in (d) are estimated from the In distribution coefficient [4] since no room temperature photoluminescence (see text) was observed from this epilayer. Note the change in vertical scale for (d). Scan area is 1 μm x 1 μm.

The root-mean-square roughness values for samples shown in Figs. 1a – 1d are 0.2, 0.4, 1.4, and 8 nm, respectively. The layers with a periodic structure (Figs. 1a – 1c) have a mirror-like appearance to the eye, and exhibit a slight 'wavy' texture under Nomarski contrast microscopy. Conversely, the layer shown in Fig. 1d is hazy to the eye. The breakdown in the growth mode from supersteps to a three-dimensional mechanism may be related to the higher x- and y-values of this sample, since they correspond to a region well within the miscibility gap [3].

Figure 2 shows HRXRD ω-2Θ scans of the $Ga_{1-x}In_xAs_ySb_{1-y}$ epilayers shown in Figs. 1a – 1c. The scans are plotted on a log scale. All layers are nominally lattice matched to the GaSb substrate, with full width at half-maximum values (FWHM) that are on the same order (23-32 arc s) as the GaSb substrate (18 arc s). Only the layer with the highest x- and y- values (Fig. 2c) exhibits some broadening, of relatively low intensity, which corresponds to a maximum lattice mismatch of only 2 x 10^{-3}.

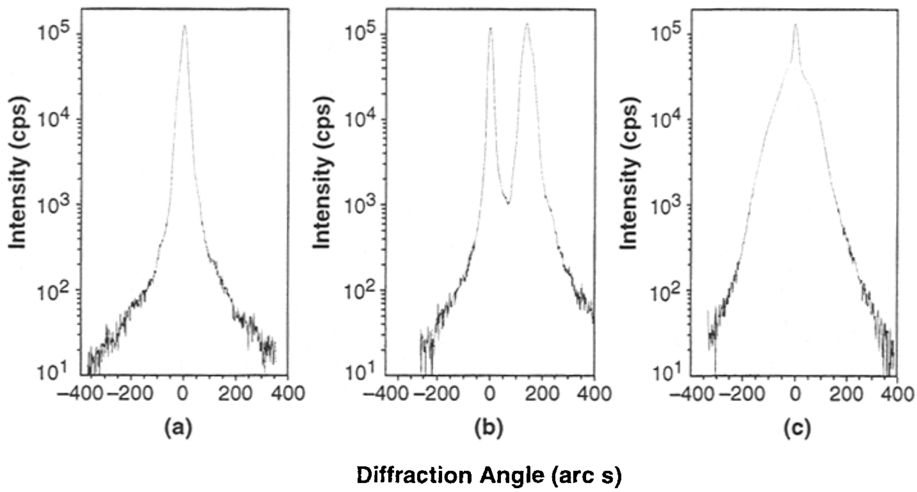

FIGURE 2. High resolution x-ray diffraction of $Ga_{1-x}In_xAs_ySb_{1-y}$ epilayers grown at 525°C on (001) 6° toward (111)B GaSb substrates with compositions: (a) x = 0.09, y = 0.08; (b) x = 0.16, y = 0.15; (c) x = 0.20, y = 0.18.

Figure 3 shows the 4 and 300 K PL spectra for $Ga_{1-x}In_xAs_ySb_{1-y}$ epilayers discussed in Figs. 2a – c. The peak emission for the sample with x = 0.09, y = 0.08 (Fig. 3a) is 1818 and 2035 nm at 4 and 300 K, respectively. The 4 K FWHM is 5.3 meV. With increasing x and y values, the 4 and 300 K emission increases to 2080 and 2320 nm, respectively, for x = 0.16, y = 0.15 (Fig. 3b); and to 2225 and 2505 nm, respectively, for x = 0.2, y = 0.18 (Fig. 3c). The 4 K FWHM also increases to 7.5 and 25 meV, respectively. Although lattice-matched $Ga_{1-x}In_xAs_ySb_{1-y}$ of higher In and As composition (see Fig. 1d) was epitaxially grown, this layer did not exhibit PL at 4 or 300 K. The longest 300 K PL emission that was observed in this study is 2525 nm, which is longer than any other values previously reported for this alloy system grown by OMVPE [3,6,7].

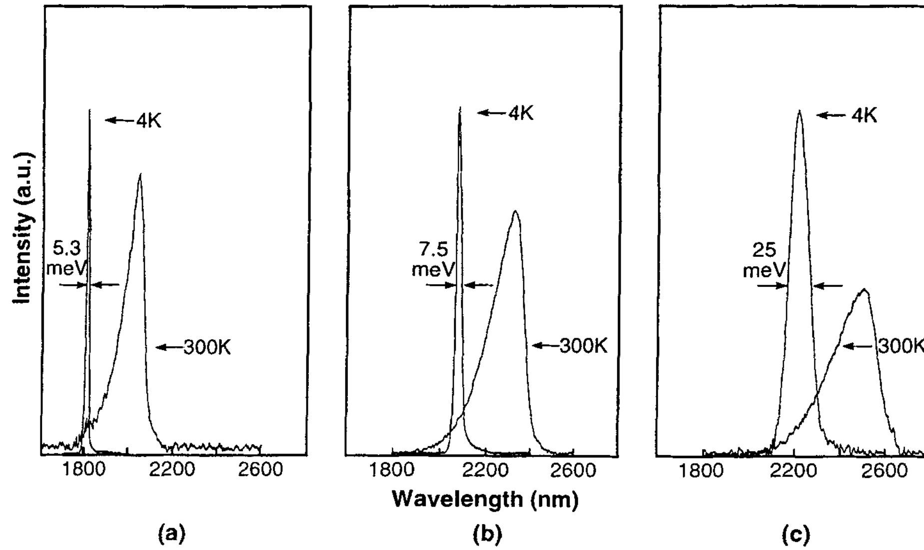

FIGURE 3. Photoluminescence spectra measured at 4 and 300 K of $Ga_{1-x}In_xAs_ySb_{1-y}$ grown on (001) 6° toward (111)B GaSb substrates. Layers were grown at 525°C: (a) x = 0.09, y = 0.08; (b) x = 0.16, y = 0.15; (c) x = 0.20, y = 0.18.

The 300 K electrical properties of p- and n-doped $Ga_{1-x}In_xAs_ySb_{1-y}$ are summarized in Figs. 4a and 4b, respectively. The plots include data for layers grown at 525 and 550°C [4] on (001) 2° toward (110) and (001) 6° toward (111)B substrates. The majority of the data, which are shown as filled circles, corresponds to layers with 300 K PL emission at ~2.25 μm. The hole concentration ranges from 4.4 x 10^{15} to 1.9 x 10^{18} cm^{-3} with mobility values between 560 and 180 cm^2/V-s, respectively. The two higher mobility values measured for p-GaInAsSb at the lower concentration ~ 8 x 10^{15} cm^{-3} are data for samples with a 0.8-μm-thick GaSb buffer layer.

The data in Fig. 4a indicate that the p-type electrical characteristics depend on the $Ga_{1-x}In_xAs_ySb_{1-y}$ alloy composition. As the x and y values increase, the mobility values decrease for comparable hole concentration. For p ~ 1 x 10^{17} cm^{-3}, the hole mobility is 441 cm^2/V-s for 2.05-μm material, compared to 239 cm^2/V-s for the 2.5-μm material. On the other hand, the data shown in Fig. 4b for n-type GaInAsSb suggest that the electrical characteristics are independent of alloy composition. The electron concentration ranges from 2.2 x 10^{17} to 3.2 x 10^{18} cm^{-3}, with corresponding mobility values between 5208 and 2084 cm^2/V-s, respectively.

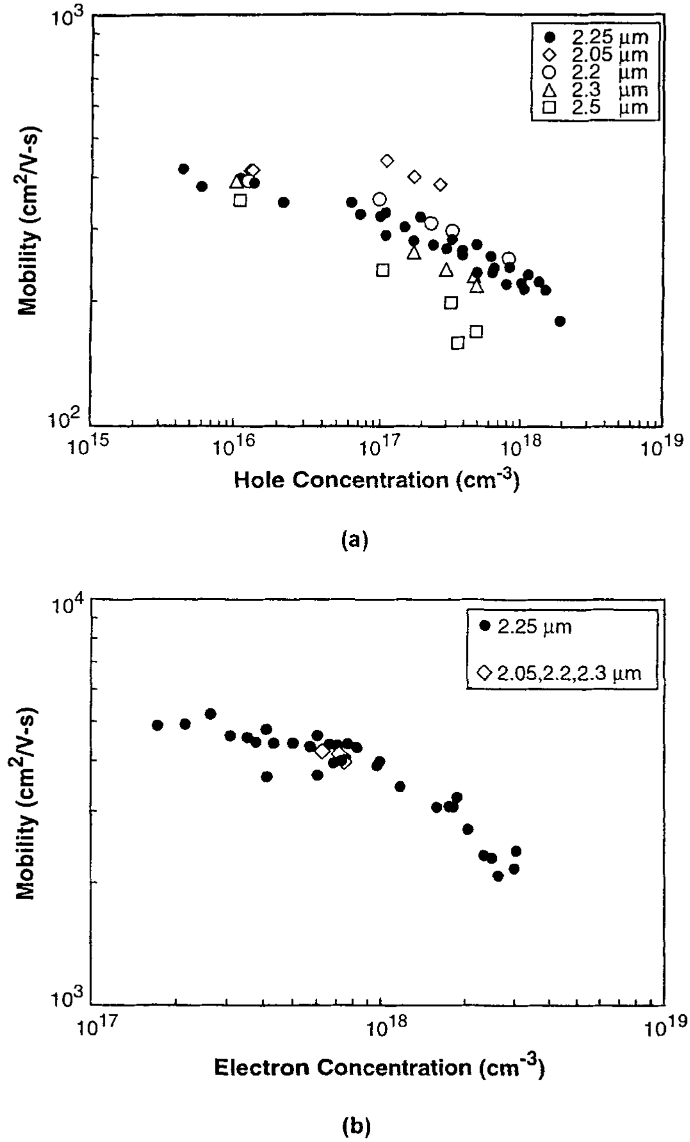

FIGURE 4. Electrical properties measured at 300 K of (a) p-GaInAsSb and (b) n-GaInAsSb.

THERMOPHOTOVOLTAIC DEVICES

GaInAsSb TPV devices were grown on (001) 6° toward (111)B GaSb substrates with a p-on-n configuration (Fig. 5). The GaInAsSb base layer is doped n-type to ~5 x 10^{17} cm^{-3} and is 1 µm in thickness, while the GaInAsSb emitter layer is doped p-type to ~2 x 10^{17} cm^{-3} and is 3 or 4 µm in thickness. The upper 0.05-µm-thick p-GaSb layer (p-doped to ~2 x 10^{18} cm^{-3}) serves as the window/contact layer. Although an AlGaAsSb window layer was incorporated previously to reduce surface recombination [1,8], a GaSb window layer was used in this study to simplify the layer structure. Thick emitter layers were incorporated to take advantage of the longer minority carrier diffusion lengths in the p-type layer [9]. Three structures with different $Ga_{1-x}In_xAs_ySb_{1-y}$ composition were grown to obtain various λ_c.

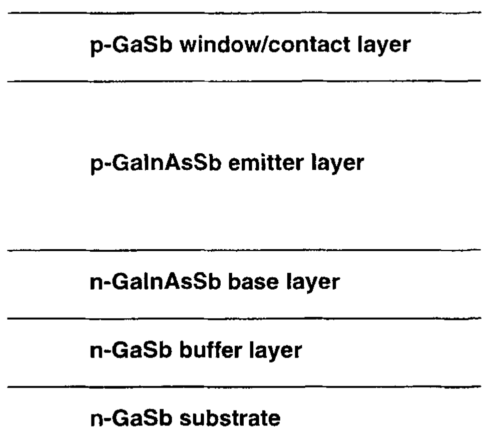

FIGURE 5. Schematic structure of GaInAsSb/GaSb TPV device. The GaInAsSb alloy composition was varied to evaluate device performance at different λ_c.

Large-area (1 cm^2) TPV cells were fabricated using a conventional photolithographic process. A single 1-mm-wide central busbar connected to 10-µm-wide grid lines spaced 100 µm apart was used to make electrical contact to the front surface. Ohmic contacts to p- and n-GaSb were formed by depositing Ti/Pt/Au and Au/Sn/Ti/Pt/Au, respectively, and alloying at 300°C. Mesas were formed by wet chemical etching to a depth of ~5 µm. No antireflection coatings were deposited on these test devices.

The external quantum efficiency QE as a function of wavelength is plotted in Fig. 6 for three TPV devices with a 4-μm-thick emitter. The λ_c ranges from 2.3 to 2.5 μm, which is the longest wavelength that has been reported for TPV devices in any materials system. A maximum QE is measured at ~1.6 μm, and is 59, 57, and 58% for devices with λ_c of 2.3, 2.4, and 2.5 μm, respectively. The QE decreases below 1.6 μm because of absorption in the GaSb window layer. The spectral response is nearly flat between 1.6 and 2.2 μm for all three devices. For the device with λ_c = 2.5 μm, the QE is as high as 41% at 2.5 μm. At 1.6 μm, the internal QE of the three devices is 91, 88, and 90%, respectively, assuming a surface reflection of 34% and absorption of 2% in the GaSb window layer. These values of QE are consistent with estimates of minority carrier diffusion lengths of ~20 μm and surface recombination velocity of ~4000 cm/s reported for lattice-matched GaInAsSb TPV devices with λ_c = 2.3 μm [10].

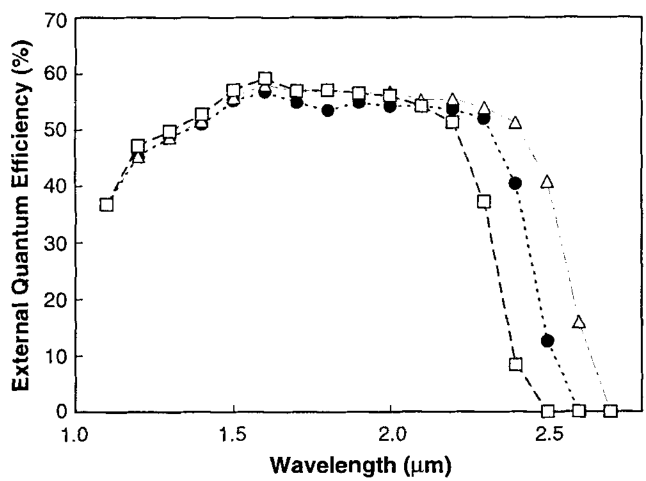

FIGURE 6. External quantum efficiency of GaInAsSb/GaSb TPV devices as a function of wavelength. The emitter thickness is 4 μm. No antireflection coatings were deposited.

Measurements of short circuit current vs open circuit voltage V_{oc} were performed at room temperature. Table 1 summarizes data for three TPV devices with various λ_c. For the 2.3-μm device, V_{oc} is 313 mV at a short circuit current density J_{sc} of 3.4 A/cm^2. This value is comparable to the value reported for TPV structures with the AlGaAsSb window layer [1,8]. With increasing λ_c, V_{oc} decreases to 269 and 239 mV for the 2.4- and 2.5-μm devices, respectively. This reduction may result from increases in dark current, Auger recombination, surface recombination velocity, or carrier trapping at the p-GaInAsSb/p-GaSb interface due to the valence band offset.

The best V_{oc} values for lattice-mismatched InGaAs/InP TPV devices are similar even though those devices had a shorter λ_c of 2.2 μm [11], thus showing the advantage of lattice-matched GaInAsSb/GaSb TPV structures. Fill factors for the GaInAsSb/GaSb devices range from 58 to 66% at current densities of ~3 A/cm^2.

TABLE 1.

DATA FOR GaInAsSb TPV CELLS UNDER ILLUMINATION

λ_c (μm)	V_{oc} (mV)	J_{sc} (A/cm^2)	FF (%)
2.3	313	3.4	66
2.4	269	3.5	62
2.5	239	3.6	58

SUMMARY

$Ga_{1-x}In_xAs_ySb_{1-y}$ epilayers were grown lattice matched to GaSb substrates by OMVPE. Room-temperature PL emission at wavelengths as long as 2.5 μm was achieved, which is the longest 300 K wavelength obtained for this alloy grown by OMVPE. Low-temperature PL spectra exhibit FWHM as narrow as ~5 meV, the smallest value reported for GaInAsSb alloys grown by OMVPE. This high optical quality of metastable GaInAsSb epilayers was achieved by using a low growth temperature of 525°C. The first lattice-matched GaInAsSb/GaSb TPV devices with extended λ_c to 2.5 μm have been demonstrated. The internal QE of these TPV devices is 90% at 1.6 μm, and as high as 62% at 2.5 μm. At J_{sc} of 3.6 A/cm^2, V_{oc} is 239 mV, with a fill factor of 58%. The high performance of these GaInAsSb/GaSb TPV devices should be especially attractive for TPV systems utilizing 1100 K radiator temperatures.

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