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G. Charache, C. A. Wang, et. al.

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GaInAsSb MATERIALS FOR THERMOPHOTOVOLTAICS*

C.A. WANG, G.W. TURNER, M.J. MANFRA, H.K. CHOI, AND D.L. SPEARS
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, MA 02173

ABSTRACT

$\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{Sb}_y$ ($0.06 < x < 0.2$, $0.05 < y < 0.18$) epilayers were grown lattice-matched to GaSb substrates by organometallic vapor phase epitaxy (OMVPE) and molecular beam epitaxy (MBE). For lattice-matched alloys, mirror-like surface morphologies were obtained by both OMVPE and MBE. The 4K photoluminescence (PL) of all layers had a full-width at half-maximum (FWHM) of less than 10 meV for PL peak emission $< 1.9 \mu\text{m}$. PL FWHM increased to 30 meV for peak emission $\sim 2.12 \mu\text{m}$ for OMVPE-grown layers. Nominally undoped layers are p-type with typical 300 K hole concentration of $\sim 9 \times 10^{15} \text{ cm}^{-3}$ and hole mobility ~ 450 to $580 \text{ cm}^2/\text{V-s}$ for OMVPE-grown layers. p- and n-type doping is reported for layers grown with either technique. The ideality factor of diode structures is ~ 2 for both techniques.

INTRODUCTION

Thermophotovoltaic systems in which thermal radiation is converted to electricity through the use of a photovoltaic cell, are experiencing revived interest as the properties of low-bandgap semiconductor materials continue to improve [1]. To achieve high utilization of thermal radiation, the semiconductor cutoff wavelength should closely match the dominant wavelength of the thermal source. For TPV systems operating in the temperature range 1100 to 1500K, the peak in emissive power varies from 1.9 to $2.6 \mu\text{m}$. This wavelength range can be satisfied by $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{Sb}_y$ alloys which can be grown lattice-matched to either InAs or GaSb substrates. However, this alloy system exhibits a large miscibility gap [2,3] which limits the equilibrium growth of stable alloys to a cutoff wavelength of $2.39 \mu\text{m}$ [4]. By using non-equilibrium growth techniques such as molecular beam epitaxy (MBE) and organometallic vapor phase epitaxy (OMVPE), metastable alloys can be grown [5,6]. In this paper, we report the growth $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{Sb}_y$ alloys by OMVPE and MBE and describe the materials properties as the alloy composition approaches the immiscibility region. We also discuss diode characteristics as they relate to the performance of TPV cells.

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EPITAXIAL GROWTH, CHARACTERIZATION, AND DEVICE FABRICATION

$\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{Sb}_y$ epilayers were grown on Te-doped GaSb or semi-insulating GaAs substrates by OMVPE and MBE. For OMVPE, solution trimethylindium (TMIn), triethylgallium (TEGa), tertiarybutylarsine (TBAs), and trimethylantimony (TMSb) were used as precursors with diethyltellurium (DETe) (50 ppm in H_2) and dimethylzinc (DMZn) (1000 ppm in H_2) as n- and p-type doping sources, respectively. Layers were grown in a vertical rotating-disk reactor with the carrier gas H_2 at a flow rate of 10 slpm and reactor pressure of 150 Torr. TEGa, TBAs, and TMSb were selected as the organometallic precursors based on their low pyrolysis temperatures and minimal tendency toward adduct formation [7]. The group III mole fraction was typically 3.5 to 4×10^{-4} which resulted in a growth rate of $\sim 2.7 \mu\text{m/hr}$. The V/III ratio was varied from 0.9 to 1.7. Substrates were (100) oriented 2 degrees toward [110]. The growth temperature was 575°C for most layers, with some layers grown at 525 or 550°C .

A solid-source MBE system with Ga, In, Sb_4 , and As_2 provided by a valved As cracker was used as described previously [8]. The growth temperature was 500 - 510°C , and the growth rate was $\sim 1 \mu\text{m/hr}$. Be was used as the p-type dopant and GaTe as the n-type dopant.

The surface morphology was examined using Nomarski contrast microscopy. Carrier concentration and mobility of GaInAsSbSb epilayers, which were grown at least $3 \mu\text{m}$ thick on semi-insulating GaAs substrates, were obtained from Hall measurements based on the van der Pauw method. Photoluminescence (PL) was measured at 4 K. Double-crystal x-ray diffraction (DCXD) was used to evaluate the structural quality and degree of lattice mismatch to GaSb substrates. The composition of epilayers was determined from the room temperature energy gap dependence on composition as reported in reference [3]. Since band-tailing effects might be significant for low-band gap alloys, the room temperature energy was estimated by subtracting 0.065 eV from the 4K PL peak energy.

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 . The I-V characteristics were measured on $500 \times 500 \mu\text{m}$ devices that were cleaved.

RESULTS

Figure 1 shows the surface morphology of $2\text{-}\mu\text{m}$ -thick $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{Sb}_y$ layers of various compositions grown by OMVPE and MBE. The growth temperature was 575°C and the V/III ratio was 1.15. The surface morphology is mirror-like to the eye for each layer. However, Nomarski contrast microscopy revealed a wavy texture, similarly reported for MBE-grown layers [6], which increased with increasing In content. A smoother morphology could be obtained by reducing the growth temperature to 550 or 525°C . The morphology for the MBE-

grown layers which was also mirror-like did not change with various alloy compositions. The layers shown here are closely matched to the GaSb substrate with a lattice-mismatch $\Delta a/a < 1.5 \times 10^{-3}$. Layers with $\Delta a/a \sim 3-4 \times 10^{-3}$ exhibited a crosshatch surface morphology. The surface morphology is sensitive to V/III as shown in Figure 2 for OMVPE layers grown with $\text{TmIn}/(\text{TEGa} + \text{TmIn}) = 0.23$. Below a minimum V/III ratio, a metal-rich surface is obtained. Increasing V/III ratio above the minimum value of 1.05 resulted in an increased surface texture.

PL spectra measured at 4K showed only a single peak. Results of full-width at half-maximum (FWHM) as a function of PL peak emission E_p are shown in Figure 3 along with data previously reported by OMVPE [5,9], MBE [10], and liquid phase epitaxy [11]. Narrow FWHM ($< 10\text{meV}$) are obtained for all layers with energy transitions below $\sim 0.64\text{ eV}$, but the PL spectra is broadened considerably for the OMVPE-grown layers with lower E_p . On the other hand, the FWHM for layers grown by MBE was not as sensitive to E_p .

DCXD scans for OMVPE-grown $\text{Ga}_{0.93}\text{In}_{0.07}\text{As}_{0.08}\text{Sb}_{0.92}$ and $\text{Ga}_{0.81}\text{In}_{0.19}\text{As}_{0.16}\text{Sb}_{0.84}$, $0.7\text{ }\mu\text{m}$ thick, are shown in Figure 4 and are compared with simulations based on the Taupin-Tagachi solution of dynamical x-ray diffraction. The scan for $\text{Ga}_{0.93}\text{In}_{0.07}\text{As}_{0.08}\text{Sb}_{0.92}$ shows Pendellosung fringes which are an indication of high structural quality. Conversely, the scan for $\text{Ga}_{0.81}\text{In}_{0.19}\text{As}_{0.16}\text{Sb}_{0.84}$ shows a broadened x-ray peak and loss of fringes, which might be an indication of alloy nonuniformity or clustering similar to observations in GaInAsSb grown near the miscibility gap [12]. Layers grown by MBE did not exhibit such x-ray broadening.

The electrical properties of GaInAsSb layers grown on SI GaAs substrates by OMVPE are shown in Figure 5. Since the lattice mismatch between GaInAsSb lattice matched to GaSb and GaAs is 8%, growth was first initiated with a GaSb buffer layer grown at 550°C . The hole concentration and mobility depended strongly on the presence of the GaSb buffer layer. These layers have a typical hole concentration of $\sim 9 \times 10^{15}\text{ cm}^{-3}$ and hole mobility ~ 450 to $580\text{ cm}^2/\text{V-s}$. Nominally undoped GaInAsSb layers grown by MBE were p-type with a hole concentration of $2 \times 10^{16}\text{ cm}^{-3}$, and hole mobility of $\sim 300\text{ cm}^2/\text{V-s}$.

The electron and hole concentration of GaInAsSb layers grown by OMVPE are shown in Figure 6 for layers doped with DETe and DMZn, respectively. The electron concentration measured at 300K ranged from $3.4 \times 10^{17}\text{ cm}^{-3}$ to $2.05 \times 10^{18}\text{ cm}^{-3}$ with corresponding mobility values of $4640\text{ cm}^2/\text{V-s}$ and $1460\text{ cm}^2/\text{V-s}$, respectively. For p-GaInAsSb, the hole concentration measured at 300K ranged from $7.8 \times 10^{16}\text{ cm}^{-3}$ to $1.5 \times 10^{18}\text{ cm}^{-3}$ with corresponding mobility values of 430 and $260\text{ cm}^2/\text{V-s}$, respectively. For MBE-grown layers, the maximum electron concentration that has been obtained is $2 \times 10^{18}\text{ cm}^{-3}$ with a mobility of

2300 cm²/V-s, and the maximum hole concentration is 5×10^{19} cm⁻³ with a mobility of 50 cm²/V-s.

Test structures that consist of p-on-n GaInAsSb epilayers were grown to evaluate junction characteristics. Figure 7 shows the I-V curve for a typical device. The ideality factor at low current levels is ~2.4. There is a relatively large leakage current at low bias, which may be related to tunnelling [13]. However, it will not affect the performance of TPV cells which operate at very high current densities. The series resistance is relatively high because of the potential barriers at the n-GaSb substrate/n-GaInAsSb and p-GaInAsSb/p-GaSb interfaces.

CONCLUSIONS

GaInAsSb epilayers were grown lattice-matched to GaSb substrates by OMVPE and MBE. For OMVPE-grown layers, a degradation in the structural and optical properties was observed as the composition of the alloy approached the miscibility gap. Layers grown by MBE, however, did not exhibit such changes. The series resistance of diode structures can be reduced by grading the interfaces and/or by heavily doping the interface regions.

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FIGURE CAPTIONS

- Figure 1 Surface morphology of GaInAsSb epilayers grown on GaSb substrates by MBE (top) and OMVPE (bottom). Various compositions as indicated.
- Figure 2 Surface morphology of OMVPE-grown GaInAsSb with various V/III ratios.
- Figure 3 Full-width at half-maximum of 4K photoluminescence spectra of GaInAsSb layers grown on GaSb substrates.
- Figure 4 Double-crystal x-ray diffraction scans of a) $\text{Ga}_{0.93}\text{In}_{0.07}\text{As}_{0.08}\text{Sb}_{0.92}$ and b) $\text{Ga}_{0.81}\text{In}_{0.19}\text{As}_{0.16}\text{Sb}_{0.84}$.
- Figure 5 Electrical properties of nominally undoped GaInAsSb as a function of GaSb buffer layer thickness: a) hole concentration and b) hole mobility.
- Figure 6 Dependence of a) electron concentration on diethyltellurium mole fraction and b) hole concentration on dimethylzinc mole fraction.
- Figure 7 I-V curve of $500 \times 500 \mu\text{m}$ p-n GaInAsSb diode structure.

Ga_{0.86}In_{0.14}As_{0.13}Sb_{0.87}

Ga_{0.93}In_{0.07}As_{0.06}Sb_{0.94}

Ga_{0.88}In_{0.12}As_{0.10}Sb_{0.90}

Ga_{0.81}In_{0.19}As_{0.17}Sb_{0.83}

20 μm

$V/III = 1.05$

$V/III = 1.65$

$V/III = 0.9$

$V/III = 1.35$

20 μm

Figure 2

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Figure 3

Figure 4a

Figure 4b

Figure 5a

Figure 5b

Figure 6a

Figure 6b

Figure 7