Thermophotovoltaic Converters Based on Poly-crystalline GaSb

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Abstract. In this work we present the development obtained on GaSb converters manufactured from GaSb polycrystals substrates since the last TPV Conference. As one of the main problem of these GaSb converters was the surface preparation, we present new surface treatments, besides higher structural quality of the ingots. The substrates were selected from polycrystalline ingots grown by vertical Bridgman technique. The electrical measurements show the n-type mobility values up to 1000 $cm^2 \cdot V^{-1} \cdot s^{-1}$. On these substrates, 4 mm^2 thermophotovoltaic cells were manufactured and characterized by illuminated J-V curves and quantum efficiency techniques.

Keywords: thermophotovoltaic cells, GaSb; polycrystalline crystals, Bridgman method.
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INTRODUCTION

Thermophotovoltaic devices in the last decades are being studied and prospected for a wide range of spatial and terrestrial applications [1-4]. Because of the operational conditions (specially emitter temperature), the most promising material for the cell converter is the GaSb and related compounds such as InGaSb, GaInSbAs, etc., due to their band gap values.

Among these materials, probably the GaSb is the most commonly used to manufacture the thermophotovoltaic converters. The GaSb has a band gap of 0.7 eV at room temperature, which shifts with the maximum power density of a common emitters used in commercial applications using fueled heat sources (range of temperature from 1200ºC to 1400ºC).

It is well known that the state of the art of GaSb crystal growth is not at the same level than other semiconductors such as GaAs, InP or Si. It is difficult to obtain single crystals without, for example twins defects, of more than 2 inches in diameter [5]. The optimal surface preparation is also a very tricky subject. It is known than there are a few companies selling GaSb substrates, in comparison with other semiconductors widely used.

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In this sense, the polycrystalline GaSb material used as a substrate for manufacturing thermophotovoltaic converters could be a very interesting subject. It is known that the preparation of a polycrystalline ingot is cheaper, easier and faster than growing a single-crystal ingot. From this point of view, the use of polycrystalline substrates should increase the production yield and should reduce the cost of fabrication.

This work is not the first that can be found on TPV converters based on polycrystalline GaSb substrates. Others authors had tried with relative good results. In 1999 TPV converters were manufactured on polycrystalline GaSb grown by Czochralski method [1]. The cell was 1.7 cm^2 in size and the average crystal size was between 0.5 – 1.0 cm^2. The cell performance was 8.7 % less in comparison with the single crystal case [1]. In 2003 other authors [6, 7] obtained similar values (V_{oc} and I_{sc}) for TPV converters made on polycrystalline and monocrystalline material, although for low voltages the influence of lower shunt resistance was visible [7].

In the last TPV Conference, the results of TPV converters manufactured on polycrystalline GaSb wafers grown by Vertical Bridgman technique were presented [8]. The cells were 2 mm^2 in size and the average crystal size was between 0.2-1.0 mm^2. The authors obtained similar I_{sc} values but lower V_{oc} and lower FF values than the values obtained for the cells on monocrystalline substrates. The main problem related with these substrates was the surface preparation which lead to high leakage currents.

In this work we continue in this direction and we present our recent developments, focused on new surface treatments for the substrates on higher structural quality ingots grown by Vertical Bridgman Technique.

SUBSTRATES: GROWTH DETAILS AND RESULTS

The GaSb ingots doped with Te were grown by the Vertical Bridgman method, growth details can be found elsewhere (see for example [8]). With this technique, the quality of the crystal depends, among other parameters, on the radial and axial temperature gradient which modifies the dopant concentration along the ingot and on the pulling rate. Experiments performed in [8] showed that higher pulling rates and dopant concentrations leads to higher polycrystallinity and higher defects concentration resulting in a reduction of the carrier mobility. With regard to the results obtained in [8], the growth of the materials used in the present work has been performed at a pulling rate of 5 mm/h with a nominal dopant concentration of 5.10^{18} cm^{-3} in a thermal gradient of about 20°C·cm^{-1}.

After growth, the ingot is cut perpendicular to the growth axis into 1 mm thick wafers and then polished with alumina powder. The polycrystalline wafers are characterized by dislocations, grain boundaries, twins, etc. In figure 1 one of the wafers used during this work is shown. The defects described above can be clearly observed.

The substrates were analyzed by Energy Dispersive X-ray Analysis using a DX4i analyzer. A slight Ga excess (51 at. %) was found. The electrical properties at room temperature (carrier mobility, type of conductivity and resistivity) were obtained by the van der Pauw technique, using a home-made Hall effect measuring system with magnetic fields up to 0.7 T. The substrates showed a n-type character, and a mobility values ranging between 500 and 1000 $cm^2 \cdot V^{-1} \cdot s^{-1}$.

FIGURE 1. Optical photography of one of the polycrystalline GaSb wafers used as substrates for the manufacturing of a thermophotovoltaic cell.

In our previous work [8] the wafers used as a TPV substrates were cleaned after the polishing process with CP4 etchant and then etched 15 s in $HF:NHO_3:H_2O$ (1:1:1). Since the results showed that a better surface preparation was needed, in this work we prepared the substrates by two alternative methods (as can be seen in Table 1), where the difference is in the last step surface treatment: the J1 substrates were cleaned in CP2 etchant ($HF:HNO_3:CH_3COOH$, 1:10:15) for 15 seconds.

TABLE 1. Summary of the process done in GaSb wafers used as a substrates for the TPV converters

GaSb:Te	Polish	Cleaned	Etched
J0 [8]	up to 0.3 μm	X	CP4 + $HF:HNO_3:H_2O$
J1	Up to 0.05 μm	X	CP2
J2	Up to 0.05 μm	X	-

In figure 2 different surface images after the treatments can be observed. It can be seen that despite of the scratch of J1 the surface is smoother than the J2 surface, where small etch pits are clearly seen.

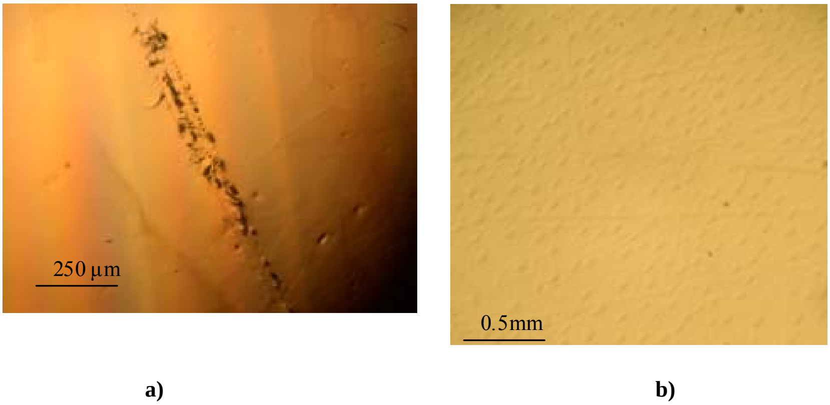

FIGURE 2. Photographs of the surface after the different treatments: a) for J1 treatment and b) for J2 treatment.

TPV CELLS: MANUFACTURE, RESULTS AND DISCUSSION

The p-n junction is formed by Zn vapour diffusion in a pseudo-closed graphite box. Prior the Zn diffusion, the substrates were cleaned with ethyleneglycol followed by methanol. The native oxide is removed with diluted HCl, so we obtain a hydrophobic surface. Immediately after and to prevent the native oxide growth the substrates are charged in a quartz ampoule inside the graphite box where an inert atmosphere is maintained. During the diffusion process an atmosphere of purified hydrogen is flowing. As it was previously reported [9] the p-layer thickness can be regulated by the temperature or the diffusion time. Because the surface of the substrates could be slightly damaged, we performed a diffusion process longer than usual, in order to have a deeper Zn profile. The Zn diffusion conditions were 75 minutes at 450ºC. In order to decrease the Zn surface concentration and the thickness after diffusion we performed successive anodic oxidations, followed by selective etchings. Finally an anodic oxidation layer is grown (165 nm thick) and maintained which can be used as antireflective coating. The back contact is formed by evaporation of AuGe/Ni/Au, annealed at 250ºC for 1 minute. The front contact is photolithographically defined, the anodic oxidation is removed by diluted HCl and after is charged in the evaporation chamber. Cr/Au/Ni/Au metals are thermally evaporated onto the GaSb surface. This contact does not need an annealing process. Finally, the cells are electrically isolated by an appropriate mesa etching.

Figure 3 shows a photograph of a polycrystlalline GaSb wafer containing several 2x2 mm^2 TPV cells array. The cells are not mechanically separated because as the substrate is polycrystalline there is not a privilege cleavage plane and a saw cutting machine can introduce strains and defects in the cells. Figure 4 presents a detail of a manufactured TPV cell. Some defects such as grain boundaries or twins can be clearly seen. It has to be pointed out that the average size of the GaSb grains are smaller than the cell area.

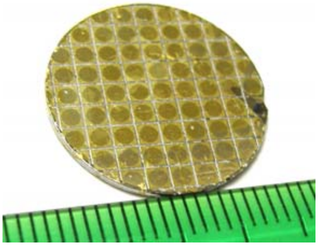

FIGURE 3. Photograph of several TPV cells array defined on polycrystalline GaSb wafer.

FIGURE 4. Among other defects, grain boundaries and twins can be clearly seen in the manufactured TPV cells.

Several cells from different substrates have been characterized by illumination J-V curves. Both values, the photogeneration current density (J_{SC}) and the open-circuit voltage (V_{OC}), are extremely low when the cells were manufactured on J2 substrates (the ones without the CP2 treatment). The illuminated J-V curve of a TPV cell made on a substrate treated with CP2 is shown in figure 5. For comparison purposes a curve of a reference TPV cell fabricated under identical conditions on commercial monocrystalline substrate has been included in figure 5. The polycrystalline cell exhibits almost the same photocurrent density (0.38 A/cm^2) but a lower open-circuit voltage (236 mV) and lower fill factor value (50%) than the values for the monocrystalline cell.

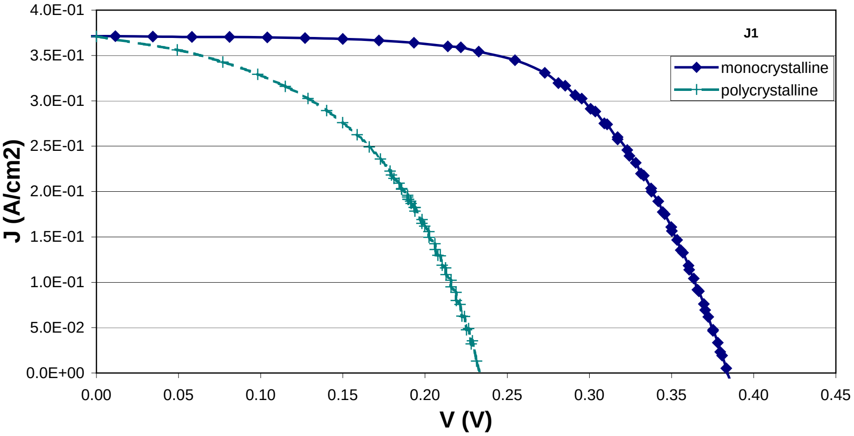

FIGURE 5. Illumination J-V curves for two cells: one manufactured on a polycrystalline wafer treated with CP2 and the other on a monocrystalline wafer.

In the same way, illuminated J-V curves were measured on different cells of a polycrystalline substrate. A wide range of J_{SC} values (from 0.2 A/cm^2 to 0.39 A/cm^2) was found, although the V_{OC} values are around 240 mV. Figure 6 presents the distribution of the cells measured over the substrate and the J-V characteristic curves can be observed. Table 2 shows the J_{SC}, V_{OC} and FF values for the measured cells. These curves show low shunt resistance leakages. In general, different Isc values are recorder over the wafer, but almost the same values of Voc. An improved value of the FF is found compared with the early data reported in [8].

The wide range of values obtained for the Jsc values along the wafer is probably related with different Zn diffusion profile [10] as the doping gradient along the wafer defines the internal electrical field which helps to collect the minority carriers and drive towards the surface.

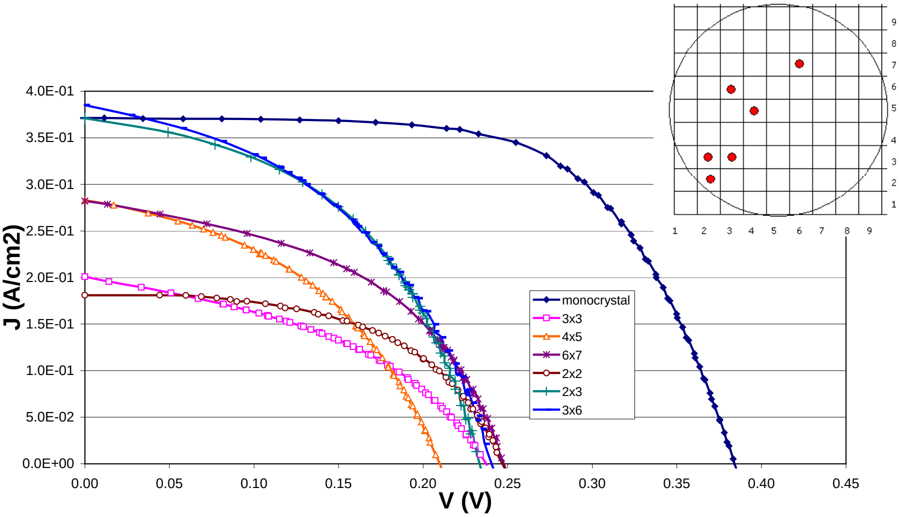

FIGURE 6. Scheme of the cells over the substrate (points indicate the measured cells) and the J-V characteristics curves.

TABLE 2. Summary of the Jsc, Voc and FF values obtained for different cells manufactured on J2 polycrystalline treated substrates

Column x Row	Voc (V)	Jsc(A/cm^2)	FF
TPV from [8]	0.240	0.36	30%
2x2	0.250	0.18	54%
3x6	0.243	0.39	45%
2x3	0.236	0.38	50%
6x7	0.251	0.28	47%
3x3	0.237	0.20	43%
4x5	0.212	0.28	44%

Zn diffusion is a well known and controlled process when the substrate is monocrystalline. The diffusion mechanism is considered to be similar to that of GaAs [11-13]. The dissolved Zn atoms occupies the Ga positions originating a shallow acceptor (Zn_{Ga}), the interstitial Zn atoms act as ionized donors (Zn^{+}_{i}), which have less solubility values than the shallow acceptor in the GaSb lattice. On the other hand the interstitial Zn atoms can kick-out a Ga atom from the lattice position (Ga_{Ga}) to interstitial sites (Ga_i), this mechanism can be expressed as:

$$Zn_i^+ \leftrightarrow Zn_{Ga}^- + Ga_i + 2h^+$$

However, Zn diffusion in polycrystalline wafers can exhibit an unexpected behavior. The different grain orientations, as well as defects in the polycrystalline substrates, specially Ga or Sb precipitation, grain boundaries, dopant inclusions [14] affects the diffusion mechanism explained above. The Zn atoms can be trapped in the grain boundaries which are randomly found. This in-homogeneous Zn distribution may affect the electric fields and therefore the minority carries distribution.

The quality of the emitter can be estimated from quantum efficiency measurements. Figure 7 shows the spectra of different TPV cells manufactured on a polycrystalline substrate and the other from a TPV cell made on a commercial substrate. At low wavelengths, where the contribution of the emitter is higher, different behaviors are observed, always lower than the monocrystalline TPV emitter. On the other hand, at high wavelengths very low values are observed indicating low lifetime of the minority carriers, low diffusion lengths and so higher dark currents.

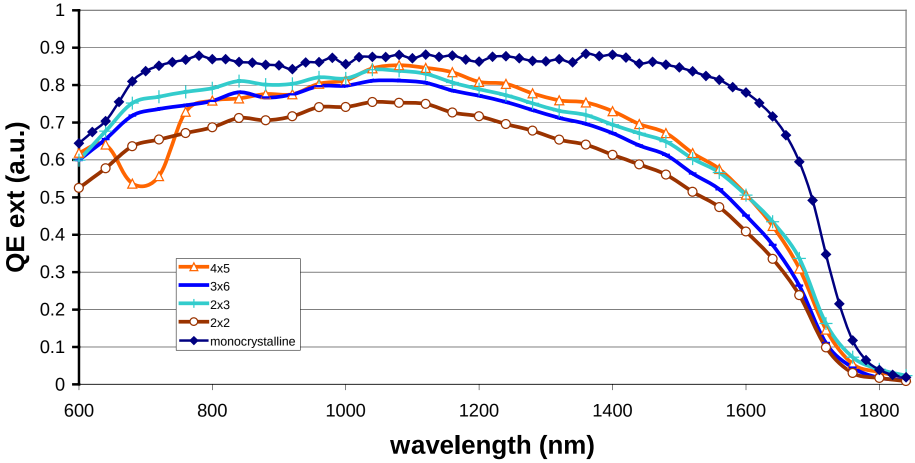

FIGURE 7. Quantum efficiency measurements for different TPV cells manufactured on a polycrystalline substrate. For comparison purpose a spectrum for a TPV cell manufactured on a monocristalline substrate is added.

CONCLUSIONS

This work presents improvements (higher FF values) on the performance of TPV cell manufactured on GaSb polycrystalline substrates grown from the melt form the Vertical Bridgman Method. This improvement is related with the surface preparation, a CP2 etchant seems to give good results. Nevertheless the Jsc and Voc values are still below the ones obtained for TPV cells manufactured on GaSb monocrystalline substrates.

Different grain orientations and grain boundaries, among other defects, are the responsible of a non-uniform Zn diffusion profile, which influence the internal electric fields and the minority carriers capture.

We propose an thermal treatment of the substrates in order to obtain a better quality prior the surface treatment.

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