Diffusion of Zn in TPV materials: GaSb, InGaSb, InGaAsSb and InAsSbP

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Abstract. This paper reviews recent results of the study of Zn diffusion from the vapor phase in important thermophotovoltaic (TPV) materials such as GaSb-, InGaAsSb-, InGaSb- and InAsSbP. Peculiarities of Zn diffusion in each of these materials and different ways of tailoring the Zn diffusion profile for fabrication of optimized emitters in TPV cells are discussed.

INTRODUCTION

Diffusion of Zn from the vapor phase is a simple and productive method of pn-junction formation in III-V materials. Especially advantageous is the pseudo-closed box diffusion method that avoids the inconvenience of sealed ampoules [1,2]. The first papers about Zn diffusion from the vapor phase into GaSb were published at the late 1960s and early 1970s [3]. Different approaches for pseudo-closed box diffusion of Zn into GaSb are described in [4,5]. L. Fraas et al was the first to apply Zn diffusion into GaSb for solar cells [6]. High-efficiency GaSb solar cells with Zn-diffused emitters developed at Boeing showed a potential of this material for infrared applications and aroused a new wave of interest for thermophotovoltaics. Also, they gave a strong impetus to the study of different antimonides for PV and TPV at many institutions worldwide.

At the present stage of development of TPV systems, TPV cells do not seem to be a bottleneck. Though their efficiency and operation parameters can certainly be improved, a much larger potential for improvement lies in other parts of a TPV system. Thus, more sophisticated TPV cells are not imperative. Actually, given a high-quality substrate material and an optimized diffused emitter, TPV cells, contrary to lasers or multi-junction space solar cells, do not require complicated epitaxially grown structures. Moreover, if epitaxial growth on high-quality substrates is not perfect, as is often the case with III-V antimonides, epitaxy can degrade TPV cell parameters. Obviously, one cannot avoid growing an epitaxial layer if no substrate is currently
available for a certain wavelength range / radiator temperature. However, even in this case, a simple one-layer epitaxial structure can be sufficient for a high-efficiency TPV cell with a diffused emitter.

In this work we studied Zn diffusion from the vapor phase in important TPV materials such as GaSb, InGaAsSb, InGaSb and InAsSbP. As was shown in several papers, optimization of diffused Zn profiles in the emitters can lead to a marked improvement of device parameters [7-10]. At the same time, there are speculations in the literature that the surface recombination in GaSb is relatively low and that this factor allows the realization of good device parameters. However, comparison of experimental and modeled data of GaSb TPV cells with diffused emitters shows that the surface recombination in GaSb is high: \( \sim 10^6 \) cm/sec [11]. Recent data on MOCVD-grown heteroface AlGaAsSb/GaSb TPV cells without the diffused emitter also showed the same value [12]. Surface recombination velocities between \( 10^5-10^7 \) cm/sec were determined on InGaSb surfaces in MOCVD-grown InGaSb structures [13]. However, despite an observed high surface recombination in GaSb, optimizing the diffusion profiles can effectively decrease its influence. We studied the following methods of the diffused Zn profile tailoring:

- Precise thinning of the as-diffused emitter that removes a dead layer with high Zn concentration (GaSb, InGaSb and InGaAsSb)
- Additional shallow Zn diffusion after the emitter thinning (GaSb, InGaAsSb)
- Shallow diffusion followed by a high-temperature annealing under SiN\(_x\) (GaSb).

Additionally, we studied the effect of anodic oxidation of a GaSb surface on Zn diffusion.

**EXPERIMENTAL**

Diffusion of Zn is performed into n-type materials. In the case of GaSb and InGaSb, single crystal or polycrystalline n-type substrates are used. Single crystal n-InGaAsSb and n-InAsSbP layers are grown by liquid phase epitaxy on n-GaSb and n-InAs substrates, respectively.

A standard horizontal slide boat technique is used for the liquid-phase epitaxial growth of the InGaAsSb and InAsSbP. The graphite slide boat is situated in a sealed quartz tube placed in a microprocessor-controlled, programmable, three-zone tube furnace. The growth ambient is palladium-diffused hydrogen at atmospheric pressure. The details of InGaAsSb and InAsSbP growth are published in [14]. Bulk crystal growth of InGaSb is described in [15].

Pseudo-closed box diffusion of Zn from the vapor phase is performed into n-type substrates or layers in a H\(_2\) atmosphere purified by a Pd cell. A specially designed multi-wafer graphite boat described in [5] is applied. Separated pure Zn and Sb vapour sources were used in more than sufficient quantities to provide the saturation of vapour pressures. In experiments with InGaAsSb and InAsSbP, an InAs- or InAs- and InP- powder is used to decrease the loss of As and P from the samples during diffusion.
It was determined for GaSb, InGaSb and InGaAsSb that the maximum (surface) Zn concentration in these materials does not depend on the diffusion temperature or Zn vapor pressure over a broad range of values. This means that the maximum Zn solubility in these materials is achieved at low temperatures/pressures. Therefore, even though it is almost certain that a Zn vapor gradient exists in a pseudo-closed diffusion boat, the same emitter profiles are obtained in different parts of the boat.

RESULTS AND DISCUSSION

GaSb

Zn diffusion from the vapor phase is performed into polished 2.5x2.5 cm$^2$ n-GaSb:Te (n=2-3x10$^{17}$ cm$^{-3}$) (100) substrates. Prior to diffusion the substrates are degassed in acetone. Afterwards, they are treated in diluted HF or HCl to remove native oxides on the surface and dried with nitrogen.

Figure 1 shows the dependence of the Zn surface concentration on the diffusion temperature for different diffusion times.

![Image](image_url)

**FIGURE 1.** Typical SIMS profiles of Zn concentration in GaSb in dependence on temperature after a 4-hour diffusion. The arrow shows the position of the kink in the Zn concentration profile for a 460°C diffusion.

It was found that Zn diffusion profiles in GaSb generally consist of 5 parts: (i) a part with a steep Zn concentration gradient near the surface, (ii) a first plateau with a relatively slow decrease of Zn concentration, (iii) a kink part (the exact position of the kink is defined as the point where the second derivative of the Zn concentration profile is at maximum), (iv) a second plateau with a relatively slow change of Zn concentration and (v) a steep diffusion front. The first part was usually thinner than 50 nm and it is not shown in Figure 1. We consider that this part of the SIMS
measurements is not reliable enough; therefore, we did not take this part into further consideration. Hereafter we define as the surface concentration the maximum concentration at the first plateau region. Our experiments have shown that Zn concentration at part (ii) - close to $1 \times 10^{20}$ cm$^{-3}$ - is too high for TPV cells. Obviously, one can expect small diffusion lengths and a strong bandgap narrowing in this part of the diffused layer and consider it to be a dead layer. Therefore, the relation of the dead layer depth to a total pn-junction depth is of interest. Figures 2 and 3 show the dependencies of the both parameters on diffusion temperature ($T$) and time ($t$), respectively. One can see that the kink depth is close to the half of the pn-junction depth.

**FIGURE 2.** pn-junction depth ($n = 3 \times 10^{17}$ cm$^{-3}$) and kink depth for 4-h diffusions of Zn into GaSb in dependence on diffusion temperature.

**FIGURE 3.** pn-junction depth ($n = 3 \times 10^{17}$ cm$^{-3}$) and kink depth for 480°C -diffusions of Zn into GaSb in dependence on diffusion time.
As a post-diffusion tailoring of diffused Zn emitter layers in GaSb, precise thinning through anodic oxidation followed by selective etching of anodic oxide is usually performed. An anodic oxidation regime with a GaSb consumption rate about 2.3 nm/V is used. The detailed description of the anodic oxidation process of GaSb is published elsewhere [16]. Through thinning of the diffused emitter in a TPV cell, a highly doped ("dead") part of the diffused layer can be removed with a high accuracy. Moreover, a second (shallow) diffusion of Zn can be performed resulting in an optimised Zn profile shown in Figure 4.

Figure 4 also shows the calculated profile of the net built-in electric field comprised of the (i) electric field $E_1$, caused by the doping gradient, and (ii) the electric field $E_2$ due to the band gap gradient caused by the effect of band gap narrowing.

The field $E_1$ moves photogenerated electrons to the p-n junction, while the field $E_2$ moves them to the surface. The resulting field has a large impact on the TPV cell parameters.

The electric field $E_1$ caused by the doping gradient between two neighbour points $i$ and $i+1$ of the SIMS-measured Zn profile can be calculated with the following expression:

$$E_1 = \frac{kT}{qd_i} \ln \frac{N_i}{N_{i+1}}, \quad (1)$$

where $d_i$ is the distance between points $i$ and $i+1$; $N_i$ and $N_{i+1}$ are doping densities at the corresponding points.

The electric field $E_2$ caused by the band gap gradient between two neighbour points $i$ and $i+1$ of the Zn profile measured by SIMS can be calculated with the following expression:

$$E_2 = \frac{A(N_i^{1/3} - N_{i+1}^{1/3})}{qd_i}, \quad (2)$$

where the coefficient $A = 10^{-8}$ eV·cm is taken from [17].

**FIGURE 4.** SIMS-measured Zn profile of the optimised p-GaSb emitter obtained as a result of three successive operations: (a) deep diffusion, (b) controlled thinning, and (c) shallow diffusion. Also shown is a calculated profile of the net built-in electric field.
One can see from Fig. 4, that if minority electrons are considered, the sweeping field is especially strong near the surface (up to 8 kV/cm), thus decreasing the influence of surface recombination on separation of photogenerated carriers.

Also, we performed a post-diffusion annealing to determine its influence on Zn profiles. After diffusion at low temperature (for example, 420°C), the surface of the diffused layer is covered with 20-50 nm thick SiNx. Afterwards, annealing in a no-Zn atmosphere at higher temperature (480-520°C) is performed. Figure 5 illustrates changes of Zn profile in an as-diffused sample after annealing. With an increase of annealing temperature and time, the maximum concentration of Zn near the surface drops, while the depth of Zn penetration increases. Such a post-diffusion treatment can be very useful for materials containing volatile components such as P and As (InAsSbP or InGaAsSb). To avoid non-congruent evaporation of P or As from unprotected semiconductor surface, one can use low-temperature initial diffusion followed by applying of a protective SiNx layer and high-temperature annealing.

![Figure 5. SIMS profiles of Zn concentration in a GaSb sample diffused at 420°C (4 h) measured just after the diffusion and after a post-diffusion annealing at 480°C (4 h) and 520°C (8 h). SiNx layer was deposited on the sample before annealing.](image)

As we have found in this work, another method to accelerate Zn diffusion and thus to avoid high diffusion temperatures and long times, is to perform Zn diffusion through the preliminary formed surface oxide. To form the oxide, we used anodic oxidation providing an oxide layer with precisely controlled parameters [16].

Figure 6 shows SIMS profiles of Zn concentration in a GaSb sample diffused through anodic oxide of different thickness. All the samples are diffused in one process, thus all other diffusion parameters are the same. One can see that the diffusion depth rapidly increases with the thickness of anodic oxide. An assumption can be made that anodic oxide increases surface absorption of Zn from the vapor phase. Similar enhanced diffusion has been observed for diffusion of Zn into GaAs through an oxidized AlAs layer [18].
FIGURE 6. SIMS profiles of Zn concentration in a GaSb sample diffused through anodic oxide of different thickness.

In a qualitative sense, the dependence of diffusion on the anodic oxide thickness might be also true for a native oxide. Thus, one can speculate that for reproducible results the thickness of the native oxide on the GaSb surface should be minimized and/or kept constant.

InGaSb

InGaSb with a band gap of 0.5-0.7 eV is of special interest for TPV applications. The availability of ternary bulk substrates would simplify the fabrication of TPV cells with band gaps lower than that of GaSb. The TPV cells could be fabricated using diffusion without expensive epitaxial steps. The antimonide-based system (InGaSb) is preferred over the arsenic (InGaAs) and phosphorus (InAsP) counterparts due to technical simplicity during growth [15].

Zn diffusion from the vapor phase is performed into polished 2 cm² n-InGaSb:Te (n = 2-3x10¹⁷ cm⁻³) substrates. These InGaSb substrates are cut from a polycrystalline boule material grown at the Rensselaer Polytechnic Institute. Prior to diffusion the substrates are degreased in acetone. Afterwards, they were treated in diluted HF or HCl to remove native oxides on the surface and dried with nitrogen.

The form of diffusion profiles of Zn into InₓGa₁₋ₓSb (Fig. 7) is similar to that in GaSb. All the major features described above for the Zn profile in GaSb can be also found in the ternary material. However, in addition to diffusion time and temperature, a new parameter – InSb content in InₓGa₁₋ₓSb – affects the Zn diffusion. As it is shown in Figure 7, an increase of InSb content in InₓGa₁₋ₓSb strongly enlarges the diffusion depth of Zn in this material. Thus, for fabrication of InₓGa₁₋ₓSb TPV cells diffusion temperatures should be essentially lower than in GaSb. Polycrystalline InₓGa₁₋ₓSb samples with x = 0.12 - 0.19 (E_g = 0.61-0.55 eV) and x = 0.26 (E_g = 0.5 eV) grown as a bulk material are studied in this work. Temperatures in the range of 430-450°C for InₓGa₁₋ₓSb samples with x = 0.12 - 0.19 are used for fabrication of InGaSb TPV cells. No TPV cells have been fabricated of InₓGa₁₋ₓSb with x = 0.26 (E_g = 0.5 eV) yet.
However, it is obvious that Zn diffusion temperatures lower than 350°C should be applied for the diffused emitter in this material.

For the tailoring of the diffused profiles anodic oxidation of InGaSb is studied. The anodic oxidation of InGaSb is performed in an electrolyte with the similar basic components as in the process developed for GaSb [16]:
(i) A component providing a suitable ionic conduction in the electrolyte. In this work we used a 5% tartaric acid aqueous solution (AAS) with a pH value $= 6.0$
(ii) A component decreasing the dissolution of the anodic oxide. In this work ethylene glycol (EG) with a volume ratio to the component (i) of 20 is used.

![Graph showing Zn concentration vs depth](image)

FIGURE 7. SIMS profiles of Zn concentration in In$_{0.5}$Ga$_{1.5}$Sb with different x in dependence on temperature after a 4-hour diffusion.

A high ratio of EG/AAS = 20 is used for InGaSb samples. In comparison, GaSb sample require EG/AAS = 5 [16]. This difference is caused by a relatively high value of the minimum current that was measured for InGaSb in electrolytes with EG/AAS = 5. Thus, it is not possible to have current densities lower than 0.3 mA/cm$^2$ for In$_{0.15}$Ga$_{0.85}$Sb and lower than 0.7 mA/cm$^2$ for In$_{0.2}$Ga$_{0.74}$Sb at an applied voltage of 90V. For comparison, minimum current densities as low as 0.01 mA/cm$^2$ are measured for GaSb at the same oxidation conditions. It is not quite clear what causes the relatively high minimum currents by the oxidation of InGaSb: higher dissolution rates of these materials, the presence of surface defects or both of them. High-quality single crystal InGaSb wafers are necessary to determine that. Since low final current densities are important for the homogeneity of anodic oxides [16], electrolytes with the lower dissolution of anodic oxides (EG/AAS = 20) are chosen.

Ellipsometry measurements of the anodic oxide thickness and refractive index are performed within an area of $5 \times 5$ mm$^2$ in 100 points. Figure 8 shows thickness of the anodic oxide of the In$_{0.15}$Ga$_{0.85}$Sb sample versus applied voltage for an electrolyte EG:AAS=20:1 and final current density $J_f = 0.1$ mA/cm$^2$. The mean values are shown together with the standard deviation. One can see that the dependence of the oxide thickness is linear. The linear fit of the measured data gives the value of the oxidation ratio equal to 2.53 nm/V. It is noteworthy that practically the same dependence of the oxide thickness on the applied voltage was observed for the In$_{0.2}$Ga$_{0.74}$Sb sample.
FIGURE 8. Thickness of the anodic oxide of the In$_{0.12}$Ga$_{0.88}$Sb sample versus applied voltage. Ellipsometry measurements of the anodic oxide thickness and $n$ were performed within an area of 5 x 5 mm$^2$ in 100 points. The mean values are shown together with the standard deviation. The dependence of the thickness of the anodic oxide of the In$_{0.26}$Ga$_{0.74}$Sb sample on applied voltage was practically the same.

For the practical use of anodic oxidation, it is important to know how much semiconductor is consumed by the oxidation. The consumption rate can be determined by performing a local oxidation, selective anodic oxide etching and measuring the step height between oxidized and non-oxidized areas. It is determined for an electrolyte with pH = 6 and EG:AAS = 20:1 that the consumption rate is 60 ± 3 % of the oxidation rate for the In$_{0.12}$Ga$_{0.88}$Sb sample and 58 ± 3 % for the In$_{0.26}$Ga$_{0.74}$Sb sample.

InGaAsSb

InGaAsSb as a quaternary alloy provides a broad variation of band gaps. For the TPV application only InGaAsSb compositions lattice matched to a GaSb substrate, for example In$_{0.15}$Ga$_{0.85}$As$_{0.17}$Sb$_{0.83}$ that corresponds to a bandgap $E_g = 0.55$ eV, are considered. The first InGaAsSb cell was fabricated at AstroPower [19]. Fully epitaxial approach was used for the fabrication of that cell. Later, in a joint work of Fraunhofer ISE and AstroPower the epitaxial emitter was substituted by the diffused one [7, 8] and higher open-circuit voltage was achieved as a result.

Zn diffusion from the vapor phase is performed into epitaxial InGaAsSb:Te ($n = 2-3 \times 10^{17}$ cm$^{-3}$) layers grown on polished 1.5 x 1.5 cm$^2$ n-GaSb:Te (100) substrates. Prior to diffusion the wafers are treated in diluted HF or HCl to remove native oxides on the surface and dried with nitrogen.

As Zn profiles in this material have a form with a kink described for GaSb, Figure 9 shows pn-junction depth, kink depth and their difference for 4-h diffusions of Zn into GaSb in dependence on diffusion temperature. Similar to InGaSb, lower than for GaSb diffusion temperatures are necessary for InGaAsSb TPV cell fabrication.

For the tailoring of the diffused layers, precise thinning through anodic oxidation and selective oxide etching, as well as additional shallow Zn diffusion after the emitter...
InAsSbP materials lattice matched to InAs or GaSb are of special interest for the TPV application. Materials with a bandgap down 0.35 eV are available in this system. There is only one publication of AstroPower reporting of an LPE-grown p-InAsSbP/n-InAsSbP/n-InAs TPV cell [20]. In [21] we fabricated a similar TPV cell with a diffused p-InAsSbP instead of an epitaxial one.

Zn diffusion from the vapor phase is performed into epitaxial InAsSbP doped with Sn or Te (n = 2-3x10^{17} cm^{-3}) layers grown on polished 1.5 x 1.5 cm^{2} n-InAs (100) substrates. Fig. 10 shows an essential difference between Zn profiles in InAsSbP and those in GaSb, InGaAsSb or InGaSb described above. First, Zn profiles in InAsSbP exhibit no kink and relatively low Zn concentration of 2x10^{18} cm^{-3}. The high concentration measured at the surface may be an artifact of SIMS. Nevertheless, and similar to GaSb and its alloys, it can be removed by anodic oxidation. In other words, there is no dead layer in Zn diffused InAsSbP (or it is very thin) and thus the design of an optimal Zn-diffused emitter might be easier.

Also, Fig. 10 shows a relatively strong dependence of Zn diffusion profiles on variation of As, Sb and P. More experiments are necessary to determine which element plays the main role in the observed dependence.

For the tailoring of the diffused profiles, anodic oxidation of InAsSbP is studied. The anodic oxidation of InAsSbP is performed in the same electrolyte that was developed for the oxidation of InGaSb (see above). A consumption rate of 1.5 nm/V was determined for InAsSbP.
FIGURE 10. SIMS profiles of Zn concentration in In$_x$Ga$_{1-x}$Sb with different $x$ after 4-hour 340°C diffusion.

CONCLUSIONS

Diffusion of Zn from the vapor phase into as GaSb-, InGaAsSb-, InGaSb- and InAsSbP using pseudo-closed system is studied.

Diffusion profiles in GaSb, InGaSb and InGaAsSb generally consist of 5 parts: (i) a part with a steep Zn concentration gradient near the surface, (ii) a first plateau with a high Zn concentration and its relatively slow decrease, (iii) a kink part, (iv) a second plateau with a relatively slow change of Zn concentration and (v) a steep diffusion front.

A tailoring of the diffused profiles in GaSb, InGaSb and InGaAsSb is necessary to use the diffused emitter in high-efficiency TPV cell. Precise thinning of the as-diffused emitter that removes a dead layer with high Zn concentration (GaSb, InGaSb and InGaAsSb) and additional shallow Zn diffusion after the emitter thinning (GaSb, InGaAsSb) are studied and found to be advantageous. Additionally, a shallow diffusion followed by a high-temperature annealing under SiN$_x$ and the influence of anodically oxidized surface on Zn profiles are studied in GaSb.

Contrary to GaSb, InGaSb and InGaAsSb, practically no dead layer is found in Zn diffused InAsSbP. Thus the fabrication of an optimal Zn-diffused emitter InAsSbP might be simpler.

The description and comparison of GaSb-, InGaSb-, InGaAsSb- and InAsSbP-based TPV cells with Zn diffused emitters are published elsewhere [21].

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