A Simple Single-Step Diffusion and Emitter Etching Process for High-Efficiency Gallium-Antimonide Thermophotovoltaic Devices

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A single-step diffusion followed by precise etching of the diffused layer has been developed to obtain a diffusion profile appropriate for high-efficiency GaSb thermophotovoltaic (TPV) cells. The junction depth was controlled through monitoring of light current-voltage (I-V) curves (photovoltaic response) during the post-diffusion emitter-etching process. The measured photoresponses (prior to device fabrication) have been correlated with the quantum efficiencies (QEs) and the open-circuit voltages in the fabricated devices. An optimum junction depth for obtaining the highest QE and open-circuit voltage is presented based on diffusion lengths (or minority carrier lifetimes), carrier mobility, and the typical diffused impurity profile in GaSb.

Key words: GaSb, Zn diffusion, thermophotovoltaic device

INTRODUCTION

The GaSb is an ideal candidate for thermophotovoltaic (TPV) energy conversion with radiator temperature close to 1,100°C. 1–5 While GaSb-based TPV power generators are commercially available, the manufacturing process of the TPV p-n junction GaSb cells has only been described in a United States patent 6 and not in the technical literature. While Ref. 1 describes both single-diffusion and dual-diffusion processes onto n-type GaSb, it does not give detailed process information. Available literature data indicate that there exists trade-offs between the single-diffusion and dual-diffusion processes. While a single-diffusion process is potentially less costly in production, there is a trade-off in the performance with cell quantum efficiency (QE) and short-circuit current versus diode leakage and cell open-circuit voltage. To get high QE, the light-absorbing layer should either have a low doping concentration (needed for high minority-carrier diffusion length) and large thickness (thick emitter device) or be shallow in depth if the doping concentration is high (typically the case with a diffused junction). 1–3,7,8 Thick emitters are advantageous because they decrease the dark current in the device because of the influence of the infinite surface recombination at the metal grid contact/semiconductor interface. On the other hand, for a low specific-contact resistance (good ohmic contact) and, thus, a high fill factor, a heavily doped emitter is required. Deep junctions are also necessary to prevent metal spiking from shorting the cell. In diffused emitters, one should also consider a complicated form of built-in electric fields generated through dopant concentration gradients and bandgap narrowing effects (typical of heavily doped semiconductors). Therefore, optimization of the emitter depth is necessary to achieve high-performance TPV cells. As will be discussed later, a high near-surface electric field resulting from a diffused impurity profile is advantageous for devices as it reduces the surface recombination velocity for minority carriers.

Several innovative approaches have been used by different researchers in the past for fabricating high-performance GaSb TPV and infrared solar
cells. Fraas et al.\textsuperscript{1,2} employed an “etch-back” technique with a single-step diffusion process to obtain high-efficiency cells. In this technique, high-temperature zinc diffusion was performed to obtain a deep junction, followed by deposition of a silicon-oxynitride diffusion-barrier layer to serve as a masking layer during thinning of the diffused junction in the active region of the cell. After cell fabrication, a dilute etchant was used to further etch the GaSb between the metal grid lines to thin the active region of the junction and increase QE. The main disadvantage of this technique is the extremely narrow etching time window for obtaining high QE. Even a 10-sec etch beyond the maximum QE results in a sharp decrease in the open-circuit voltage and fill factor of the cells.\textsuperscript{2}

Fraas et al.\textsuperscript{6} and Gruenbaum et al.\textsuperscript{3} employed a two-step diffusion process with multiple photolithography steps. In this method, a shallow diffusion initially creates the active region of the cell. Thereafter, a diffusion barrier layer of silicon oxynitride is deposited and windows etched in regions where metal line grids are to be deposited. Then, a second, high-temperature, deep-diffusion process provides a deep diffusion in the window regions. This process did not alter the p-type regions in the active areas; only the regions under the metal grids possess heavy doping with deep junctions.

Recently, Sulima et al.\textsuperscript{7} developed an alternative two-step diffusion process for high-performance cells that is simpler than the approach of Gruenbaum et al.\textsuperscript{3} In this technique, a high-temperature deep diffusion is first performed with the emitter precisely thinned using anodic oxidation. The thickness of the junction is sufficient to avoid metal spiking through the junction. Hence, the emitter is thicker than that of Gruenbaum et al.\textsuperscript{3} but lightly doped. A short, second diffusion step is employed to create a sharp zinc profile and, hence, a strong electric field in the near-surface region. The large near surface reduces the effective surface recombination drastically. The technique adopted by Sulima et al.\textsuperscript{7} does not require any photolithography step during the diffusion cycle. It was also shown that if the emitter is etched carefully to reach a point where the plateau in the diffusion profile is completely removed, good devices could be fabricated using a single-step diffusion process.

To take advantage of the high near-surface electric fields, we have developed a method for monitoring and controlling the junction depth during the emitter-etching process (after single-step diffusion). Our GaSb TPV cell-fabrication scheme consists of (a) single-step zinc diffusion from the vapor phase, (b) a multistep diffused-layer etching process using ammonium sulfide, (c) photovoltaic measurements at a constant current after each etching cycle, and (d) a front and back side metallization process after the photovoltage of the diffused sample reaches a near-maximum value. The maximum photovoltage is obtained when the junction is shallow and a high electric field is present in the near-surface region. Etching beyond this junction depth results in a drastic decrease in photovoltage until the entire diffused layer is removed.

A key feature of our approach is the diffused-junction screening procedure prior to cell fabrication and the controlled etching by ammonium sulfide. By monitoring the photovoltage during emitter thinning, both the criteria for getting high-efficiency cells, namely, the high electric field in the near-surface region, and a suitable diffused-layer thickness (to avoid metal spiking) are assured. The photovoltage monitoring technique also compensates for any variations in either diffusion depth from cycle-to-cycle (or sample-to-sample) or etchant strength, so that cells fabricated from different batches will have more similar performance. Moreover, the present method appears less sensitive in terms of etching time for maximum QE or lowest dark currents (and highest open-circuit voltage). In this paper, we present our diffusion and emitter etching process. Characteristics of fabricated TPV cells are briefly presented to demonstrate the reliability of the new process.

**EXPERIMENTAL DETAILS**

Zinc diffusion was performed in n-GaSb substrates (Te doped) using the leaky box technique.\textsuperscript{3-9} The n-GaSb wafers, $<100>$ oriented from Wafer Tech. Ltd. (Payson, AZ, USA) with a carrier concentration of $2\times10^{18}$ cm$^{-3}$, were diced to $1.5\times1.5$ cm$^2$. Prior to diffusion, the GaSb wafers were degreased in xylene, acetone, and methanol, followed by etching the native oxide layer in HCl. Diffusion was carried out in a pseudo-closed graphite box with the GaSb wafer placed above the zinc pellet (approximately 1 cm away). Diffusion temperatures and times were in the range of 450–550°C and 2–6 h, respectively. Prior to any series of diffusion experiments, the graphite was baked at 900°C for 24 h under vacuum ($\approx 10^{-6}$ torr), and the zinc pellets were etched in HCl. High-temperature baking was found to be crucial for ensuring high-quality mirror-shiny surfaces of the wafers after diffusion. After the high-temperature baking, the boat was saturated with zinc in one to two initial experiments to create a uniform, zinc vapor pressure over the wafer surface. Between successive diffusion experiments, the boat was stored in the diffusion chamber in an argon-hydrogen ambient. The TPV cell-fabrication process (such as front and back side metallization, lift-off scheme, and mesa etching) and cell characterization and testing were identical to that reported earlier.\textsuperscript{10}

**RESULTS AND DISCUSSION**

For the present investigation (baseline process), Zn diffusion was performed at 500°C for 5 h. Once the boat is sufficiently saturated with zinc (in the first few experiments after baking), a junction depth of $\approx 0.6$ μm is obtained with the preceding condition. After diffusion, the boat was rapidly cooled to room
temperature. Post-diffusion emitter etching was performed using an ammonium sulfide \([\text{NH}_4\text{S}_x]\) solution, which has also been shown to etch III–V compounds at a slow rate\(^{11-14}\) apart from passivating the surface dangling bonds.\(^{15}\) For a properly stirred solution, a uniform etch rate of 0.2 nm/sec has been observed for GaSb. The etching rate was determined by the Alpha Step surface profilometer (KLA-Tencor, San Jose, CA, USA). Preferential etching was performed by masking a portion of the sample by Apeizon W wax (Apeizon Products, Manchester, U.K.). After etching, the wax was dissolved in xylene, and the surface profile measured. The junction depth was measured by determining the surface conductivity type (using the hot-point probe method) after each etching cycle.

Figure 1a shows a typical zinc profile in GaSb (diffused at 500°C for 5 h) obtained from secondary ion mass spectrometric (SIMS) measurements. Figures 1b and c show the zinc profiles in the samples etched in ammonium sulfide for 29 min and 55 min, respectively.

To monitor the junction depth during the post-diffusion emitter etching, photovoltage measurements were performed using a two-point probe setup.\(^9\) The diffused sample was placed on a metal block, and the top surface was contacted with a metal point probe. The current-voltage (I-V) characteristics in the low current regime were observed using an oscilloscope. A tungsten lamp was used to illuminate the sample, and the shift in I-V (the photovoltage) was measured. The photovoltage generated by illuminating a constant intensity of light depends on the junction depth and the surface electric field. The surface electric field is generated by the impurity doping profile (zinc concentration gradient). A typical photovoltage profile as a function of cumulative etching times is shown in Fig. 2a. As-diffused samples (unetched) exhibit photovoltages in the range of 10–20 mV. In the initial stages of etching, the photovoltage increases slowly (Fig. 2a). This is followed by a rapid increase; beyond the maximum value (~250 mV), the photovoltage decreases drastically until the junction is reached. The maximum photovoltage corresponds to a thin emitter with surface zinc concentration (Fig. 1c) an order of magnitude lower than in the as-diffused sample (Fig. 1a). As will be described in the next section, the external QE increases with the decrease in emitter depth, whereas the open-circuit voltage \(V_{oc}\) decreases. Hence, it is essential to optimize the junction depth for achieving maximum power output instead of either higher QE or \(V_{oc}\). The photovoltage measurements can be used as an invaluable tool for monitoring the junction depth so that cells fabricated in different batches will have similar performance, irrespective

![Graph of Concentration vs. Depth](image1)

**Fig. 1.** The zinc profiles in n-GaSb diffused at 500°C for 5 h (as determined using the SIMS technique): (a) as-diffused sample and (b) and (c) after etching the diffused sample in ammonium sulfide for 29 min and 55 min, respectively.

![Graph of Photovoltage vs. Etching Time](image2)

**Fig. 2.** (a) The photovoltage versus etching time for the GaSb p-n junction during the emitter thinning process using an ammonium sulfide solution, (b) QE, and (c) \(V_{oc}\) in the fabricated TPV cells versus the photoresponse measured in the samples after diffusion and emitter thinning.
of any unintentional variations in diffusion depths (during diffusion cycle) or etchant strength. From the experimental plots of external QE in the cell versus the final photovoltage of the diffused and etched junction (Fig. 2b) and a similar plot (Fig. 2c) for the $V_{oc}$, it has been ascertained that a photovoltage of 100–150 mV will result in the best GaSb TPV cell.

The QEs and I-V characteristics for the two 1-cm$^2$ area GaSb cells (samples 4 and 5) fabricated using the single-step diffusion and etching technique (with zinc profiles as shown in Fig. 1b and c) are shown in Fig. 3a and b, respectively. The values of QEs and dark currents are amongst the best reported for GaSb TPV cells. It is important to note that there is a one-to-one correlation between the I-V and emitter depth (as seen from SIMS). Even though the external QE is identical for the cells, a thinner junction results in an increase in leakage current (and, hence, a decrease in open-circuit voltage). There is an optimum emitter depth to obtain the highest QE and lowest leakage current. If the emitter is thick, the external QE will decrease because of the high doping concentration in the emitter region, which decreases the minority carrier lifetime (Fig. 4a). On the other hand, if it is too thin, the leakage current increases, which decreases the $V_{oc}$ (Fig. 4b). The optimum emitter thickness to obtain the highest QE with lowest leakage current is dependent on the zinc profile. With the present single-step diffusion profiles and etching technique, the optimum junction depth for the best GaSb cell performance is estimated to be between 0.3 μm and

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**Fig. 3.** (a) The QEs and (b) I-V characteristics of the zinc-diffused GaSb TPV cells with diffusion profiles shown in Fig. 2b and c.

**Fig. 4.** (a) The external QE and (b) $V_{oc}$ versus emitter depth for GaSb TPV cells.
0.5 µm. Further improvement can be obtained by two-step diffusion\textsuperscript{6} but that increases the process complexity.

Apart from the high electric fields in the near-surface region, another key factor in obtaining low dark currents or high open-circuit voltage is speculated to be the absence of oxygen at the p-n junction interface in these samples. The SIMS profiles of a sample diffused at 500°C for 2 h show extremely shallow diffusion depths for oxygen, which is etched off during the emitter thinning process. The oxygen concentration falls from $10^{21} \text{cm}^{-3}$ near the surface to less than $10^{18} \text{cm}^{-3}$ within 0.15 µm and is at the background level ($< 5 \times 10^{17} \text{cm}^{-3}$) near the junction. Oxygen is a deep impurity in III-V compounds, and its presence in high concentration at the p-n interface can be deleterious for devices (recombination center). The extremely shallow oxygen diffusion depth in the diffused samples is a result of a contamination-free boat and environment during diffusion. This has been quantified in our preliminary diffusion studies wherein an insufficiently baked graphite boat resulted in enhanced oxygen contamination in the diffused samples.

**CONCLUSIONS**

In summary, we have been able to demonstrate high-performance GaSb TPV cells from bulk substrates using a single-step zinc-diffusion and emitter-etching technique monitored through photovoltage measurements. The emitter thinning and photovoltage monitoring prior to cell fabrication has the advantage for compensating any cycle-to-cycle or wafer-to-wafer variations. In spite of the simple technology, the characteristics of the fabricated cells are similar to the best cells reported. Ammonium sulfide has been found to be a suitable etchant for emitter thinning with a stable etching rate of 0.20 nm/sec. The effect of junction depth on the power output has been studied. Emitter depth in diffused junction cells necessary for maximum power output from GaSb has been estimated to be approximately 0.4 µm.

**REFERENCES**