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A Simple Single Step Diffusion And Emitter Etching Process For High Efficiency Gallium Antimonide Thermophotovoltaic Devices

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Abstract:

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 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 and the open circuit voltages in the fabricated devices. An optimum junction depth for obtaining highest quantum efficiency and open circuit voltage is presented based on diffusion lengths (or minority carrier lifetimes), carrier mobility and typical diffused impurity profile in GaSb.

Keywords: GaSb, Zn diffusion, thermophotovoltaic device

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1. Introduction

GaSb is an ideal candidate for thermophotovoltaic (TPV) energy conversion with radiator temperature close to 1100 °C [1-9]. While GaSb-based TPV power generators are commercially available, the manufacturing process of the TPV p-n junction GaSb cells is quite complex, involving multiple diffusions and related processing [5-9,11]. For high performance cells, the complexity in the fabrication process arises due to the need for tailoring the diffused impurity profile in the emitter [5-11]; to reduce cost of production, single-step diffused p-n homojunctions are preferred.

The junction technology is based on zinc diffusion in n-GaSb substrates (Te- doped), thereby creating a p-type emitter layer [5-11]. The typical zinc profile after a single step diffusion process consists of a heavily doped near-surface region, followed by a plateau and a graded region near the metallurgical junction. There are several requirements for obtaining high quantum efficiency, low dark current and high fill factor. Some of them are counteractive. For high quantum efficiency, 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) [5-11]. Thick emitters are advantageous because they decrease the dark current in the device due to 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 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 band gap narrowing effects (typical of heavily doped semiconductors). Therefore, optimization of the emitter depth is necessary in order to achieve high performance TPV cells. As will be discussed later, a high near surface electric field resulting from 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 [5-11] in the past for fabricating high performance GaSb TPV and IR solar cells. Fraas et al. [5,6] 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 quantum efficiency. The main disadvantage of this technique is the extremely narrow etching time window for obtaining high quantum efficiency. Even a 10 second etch beyond the maximum quantum efficiency results in a sharp decrease in the open circuit voltage and fill factor of the cells [6].

Gruenbaum et al. [7] 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. [10] developed an alternative two-step diffusion process for high performance cells, which is simpler than the approach of Gruenbaum et al [7]. 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. [7], 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. [10] 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 a single step diffusion). Our GaSb TPV cell fabrication scheme consists of: (a) single step zinc diffusion from the vapor phase, (b) a multi-step diffused layer etching process using ammonium sulphide, (c) photovoltage measurements at 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. By monitoring the photovoltage during emitter thinning, both 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 quantum efficiency or lowest dark currents (and highest open circuit voltage). In this paper, we present our diffusion and emitter etching process. Characteristics of TPV cells fabricated 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 [7-12]. The n-GaSb wafers, <100> oriented from Wafer Tech. Inc. with carrier concentration of $2 - 4 \times 10^{17} \text{ cm}^{-3}$, were diced to $\sim 1.5 \times 1.5 \text{ cm}^2$. 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 1cm away). Diffusion temperatures and times were in the range of 450 – 550 °C and 2 to 6 hours, respectively [12]. Prior to any series of diffusion experiments, the graphite was baked at 900 °C for 24 hours under vacuum ($\sim 10^{-6}$ 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 argon-hydrogen ambient.

Results and Discussion:

For the present investigation (baseline process), Zn-diffusion was performed at 500 °C for 5 hours. Once the boat is sufficiently saturated with zinc (in the first few experiments after baking), a junction depth of $\sim 0.6 \mu\text{m}$ is obtained with the above condition. After diffusion the boat was rapidly cooled to room temperature. Post diffusion emitter etching was performed using ammonium sulphide $[(\text{NH}_4)_2\text{S}_x]$ solution which has also been shown to etch III-V compounds at a slow rate [13-16] apart from passivating the surface dangling bonds [17]. For a properly stirred solution, uniform etch rate of 0.2 nm/sec has been observed for GaSb. The etching rate was determined by the Alpha Step surface profilometer. Preferential etching was performed by masking a portion of the sample by Apeizon W wax. 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 hot point probe method) after each etching cycle.

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

To monitor the junction depth during the post diffusion emitter etching, photovoltage measurements were performed using a two-point probe set-up [12]. 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 Figure 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 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 (Figure 2b) and a similar plot (Figure 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 TPV cells fabrication process (such as front and back side metallization, lift-off scheme, mesa etching) and cell characterization and testing were identical to that reported earlier [18].

The quantum efficiencies and I-V characteristics for the two GaSb cells (samples 4 and 5) fabricated using the single step diffusion and etching technique (with zinc profiles as shown in Figs. 1b and 1c) are shown in Figures 3a and 3b, respectively. The values of quantum efficiencies 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 are 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 due to the high doping concentration in the emitter region, which decreases the minority carrier lifetime (see Fig. 4a). On the other hand, if it is too thin, the leakage current increases which decreases the V_{oc} (as shown in 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 approximately 0.4 μm .

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 show extremely

shallow diffusion depths for oxygen (in these samples), which is etched off during the emitter thinning process. 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.

Conclusion:

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 cells fabricated are similar to the best cells reported. Ammonium sulphide 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 .

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Figure 1. Zinc profiles in n-GaSb diffused at 500 °C for 5 hours (as determined using secondary ion mass spectrometric (SIMS) technique): (a) as-diffused sample, (b) and (c) after etching the diffused sample in ammonium sulphide for 29 min and 55 minutes, respectively.

Figure 2. (a) Photovoltage versus etching time for GaSb p-n junction during the emitter thinning process using ammonium sulphide solution, (b) QE and (c) V_{oc} in the fabricated TPV cells versus the photoreponse measured in the samples after diffusion and emitter thinning.

Figure 3. (a) Quantum efficiencies and (b) I-V characteristics of the zinc diffused GaSb TPV cells with diffusion profiles shown in Figs. 2b and 2c.

(a)

(b)

Figure 4. (a) External QE and (b) V_{oc} versus emitter depth for GaSb TPV cells